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Introduction to the Thermodynamically Constrained Averaging Theory for Porous Medium Systems

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Preface

In recent years, the range and complexity of porous medium flow and transport problems of interest has increased dramatically. Problems in the environment involve water, gases, dissolved contaminants, and organic phases. They arise in agriculture, hydrology, and petroleum engineering in regions ranging from the deep subsurface to the near surface. In engineered systems, the behavior of filtration systems, fuel cells, and chemical reactors are described as porous medium systems. Other porous medium applications include diverse fields of study such as plant physiology, cancer tumor growth and treatment, and tomography. Interest in these problems has created a need to be able to describe multiphase problems with a relatively slow moving solid phase at a range of spatial scales. The thermodynamically constrained averaging theory (TCAT) has been developed to address this need.

TCAT is different from other scale-change methods because it assures full compatibility of problem descriptions at small scales and the larger length scales. Included in the analysis are formulations of dynamic equations for phases, interfaces between phases, common curves where interfaces come together, the geometric evolution of spaces occupied by and between phases, and thermodynamics. The larger scale descriptions are obtained in every case from averaging of smaller scale descriptions. These equations are then employed in their own right and used to formulate an entropy inequality that guides closure of the equations.

This book is an introduction to the TCAT framework. It contains all the elements of TCAT, but the applications considered are restricted to relatively simple cases. Because interscale consistency of all variables is mandated, significant explicit notation is employed to facilitate identification of the variables. Thus careful attention is paid to sorting through the subtleties of the notation so that the resultant equations can be seen to be both rigorous and meaningful.

The book consists roughly of two parts. The first half is focused on smaller scale continuum formulations of conservation and thermodynamic equations for phases, interfaces, and common curves. In the second half, tools for changing the scales of the equations are developed, the tools are used to derive foundational components of the theory, and the foundational components are used in turn to obtain closed models at a larger scale for a range of applications.

Specifically, Chap. 1 contains a qualitative overview of the elements of the TCAT method that will be employed quantitatively in the subsequent chapters. Chapters 2–5 are a self-contained presentation of principles needed for analyses at a length scale where phases are treated as being juxtaposed. Conservation equations for material in phases, interfaces, and common curves are developed in Chap. 2. These equations, applied to phases, are the ones usually encountered at a small continuum scale. The full dynamic equations for interfaces and common curves are an extension of the typical formulations. The conservation equations are developed for species that comprise an element of the system as well as for the elements as a whole. In Chap. 3, classical irreversible thermodynamics is developed for each of the constituents of a porous medium system. In Chap. 4, variational analysis is used to derive conditions of equilibrium for the system at the continuum scale. The variational techniques employed are derived in Appendix A. In Chap. 5, the equations and conditions developed in Chaps. 2–4 are combined to derive a closed equation set for a fluid phase. In this chapter, the approach to obtaining closure relations for a porous medium system is demonstrated, but by examining only a single fluid phase, the analysis is greatly simplified.

In Chaps. 6–11, the mathematical and physical considerations needed for analysis of systems at a larger scale, referred to as the macroscale, are provided. At this scale, the system is conceptualized as being composed of overlapping continua. In Chap. 6, the mathematical tools for scale change, derived in Appendix B, are applied to the conservation equations to obtain larger scale continuum equations. Averaging is applied in Chap. 7 to the thermodynamic relations, leading to a macroscale thermodynamic formalism that is unique to TCAT and fully consistent at the larger scale and between scales. The small scale equilibrium conditions of Chap. 4 are also averaged so that equilibrium conditions are expressed in terms of macroscale variables. In Chap. 8, evolution equations are developed to describe the volume fractions of each phase and other geometric variables that, on average, describe the distribution of phases within an averaging region. The changes in these variables, which do not exist at the smaller scale and cannot be described by conservation equations, are described based on averaging theorems. In Chaps. 9–11, examples are presented of application of the equations developed in Chaps. 6–8 to the description of porous medium systems: single-fluid-phase flow is considered in Chap. 9; chemical species transport in single-fluid-phase flow is developed in Chap. 10; and models for two-fluid-phase flow are derived in Chap. 11. The work in these latter three chapters to derive the desired forms requires substantial mathematical manipulations, which are detailed in Appendix C.

After working through these chapters, and the exercises at the ends of the chapters, one should have a firm grasp of the art and science of the TCAT approach. The method can then be applied by the reader to more complex systems. Chap. 12 presents a forward thinking discussion of some of the challenges and possibilities for confirming the mathematical descriptions that arise from TCAT and for supporting the discovery of parameter values in closure relations. Thus, we consider the entire text to be introductory in that it opens the door to systematic TCAT analysis and application but only hints at the applications that can be studied.

The methodologies described here have been developed by the authors with input obtained from many members of the scientific community. In particular, Professor D. Andrew Barry of EPFL has taken on the often difficult task of serving as journal editor for the reviews and publication of many of the research aspects of this work. The mostly anonymous authors of the thorough and challenging reviews that were obtained were very helpful in identifying aspects of the work that needed clarification and further development. We have been fortunate over the years to work with excellent students at the University of North Carolina (UNC) at Chapel Hill who both took our courses and contributed to the research. We also offered a series of short courses to students at the University of Stuttgart at the invitation of Professor Rainer Helmig, who has been an enthusiastic supporter of this work. Professor Helge K. Dahle of the University of Bergen has also provided encouragement for this work and opportunities to engage in enlightening and encouraging technical discussions on implementation of TCAT. These educational experiences, highlighted by the insights and commitment of students, encouraged us to develop TCAT so that it will be a more accessible analysis tool.

We have benefited from the efforts of additional collaborators. Professor Jan Prins of the Computer Science Department at UNC Chapel Hill has contributed expertise enabling the development of efficient, large-scale simulators of microscale systems. These simulators have been used to develop our mechanistic understanding and to support the functional forms of closure relations advanced in this work. The applied mathematics group at UNC Chapel Hill has supported this work intellectually and through numerical methods and analysis collaborations, especially Professors David Adalsteinsson, M. Gregory Forest, Jingfang Huang, and Richard McLaughlin. Professor Dorthe Wildenschild of Oregon State University has worked tirelessly to develop and apply high-resolution imaging methods that have informed our understanding and helped guide our theoretical work. Professor Laura J. Pyrak-Nolte of Purdue University has similarly contributed her expertise in micromodel experimental methods that have honed our thinking. Professor Tim Kelley and his group at North Carolina State University have contributed expertise in numerical methods to implement and evaluate TCAT models. Professor Bernhard A. Schrefler of the University of Padova has been an invaluable colleague, particularly in regard to solid mechanics and in implementing TCAT models for simulation of biological problems. Professor Kolumban Hutter, editor of the AGEM^2 series, has provided perceptive comments on our manuscript, and his unflagging and selfless support for this project is greatly appreciated.

The authors have made every attempt to eliminate typographical and conceptual errors and misstatements from the text. We are resigned to the fact that those efforts have not been completely successful. We acknowledge the heroic efforts of Ms. Robin Whitley in providing a careful proofreading of the text we prepared. Unfortunately, the authors retain ownership of all surviving typos, malapropisms, and stray notational markings.

The authors wish to acknowledge research funding that has been provided during the years it has taken to develop the TCAT methodology. In particular we wish to note support from the U.S. National Science Foundation, the Basic Energy Sciences

Program of the U.S. Department of Energy, and the Superfund Research Program of the U.S. National Institute of Environmental Health Sciences. The University of Bergen provided WGG an incomparable environment for working on this text using support obtained from the International Research Training Group Non-linearities and Upscaling in Porous Media (NUPUS) grant provided by the Norwegian Research Council and from a guest researcher grant through the University of Bergen Akademia agreement with Statoil. The University of North Carolina at Chapel Hill has provided support to CTM through his appointment as the Okun Distinguished Professor of Environmental Engineering and an environment that has enabled the completion of this effort.

The authors would be terribly remiss not to mention the supportive environments for this work encountered at home that involved many late nights, long weekends, and distractions from social duties. Environments unconstrained by averages, fostered by unlimited forbearance on the part of Genny Gray and Cherie Smith-Miller, were beyond any reasonable expectation and are more than gratefully appreciated.

Chapel Hill, NC
December 2013

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Contents

Notation

Notation for variables in the text. Equation numbers are provided where unique averages of macroscale quantities are defined and in other instances where deemed helpful. Definitions are not provided for some terms that are used in context-specific circumstances.

A	chemical species in a ternary A-B-C system
$A_{k\alpha}$	microscale affinity of reaction k in entity α, Eq. (5.37)
$A^{k\alpha}$	macroscale affinity of reaction k in entity α, Eq. (10.31)
$A^*_{k\alpha}$	extended microscale affinity of reaction k in entity α, Eq. (5.38)
$\overline{A}$	partial mass area
$\hat{A}^n$	interfacial velocity coefficient relating to n-phase velocity
$\hat{A}^w$	interfacial velocity coefficient relating to w-phase velocity
$\mathbb{A}$	general extensive area
$\hat{\mathbf{a}}_w$	fourth-order tensor, Eq. (5.57)
$\hat{\mathbf{a}}^{(n)}$	coefficient tensor of order n
$\hat{a}$	equation coefficients
B	chemical species in a ternary A-B-C system
$\hat{B}^n$	common curve velocity coefficient relating to n-phase velocity
$\hat{B}^w$	common curve velocity coefficient relating to w-phase velocity
b	entropy body source density
C	chemical species in a ternary A-B-C system
$\mathbf{C}$	Green's deformation tensor, Eq. (3.130)
$\mathbf{C}^s$	macroscale Green's deformation tensor, Eq. (7.17)
$\overline{\mathbf{C}}$	partial mass Green's deformation tensor, Eq. (3.180)
$\mathbb{C}_P$	heat capacity at constant pressure
$\mathbb{C}_V$	heat capacity at constant volume
$\hat{c}$	closure coefficient
$\hat{c}^{ss}$	closure coefficient introduced in Eq. (11.91)
$\hat{c}^{wn}$	closure coefficient introduced in Eq. (11.90)
$\hat{c}^{wns}$	closure coefficient introduced in Eq. (11.94)
D	reactant species, Eq. (10.70)

D	divergence theorem
$\hat{\mathbf{D}}_{AB}^{\alpha}$	binary macroscale diffusion tensor for species A and B in entity α, Eq. (10.65)
$\hat{\mathbf{D}}$	diffusion tensor, Eq. (5.69)
$\hat{D}$	diffusion coefficient, Eq. (5.70)
$\mathcal{D}$	set of material derivatives, e.g., Eq. (5.26), Eq. (9.23)
$\mathbf{d}_{i\alpha}$	microscale rate of strain tensor based on species velocity $\mathbf{v}_{i\alpha}$, Eq. (2.16)
$\mathbf{d}'_{i\alpha}$	microscale surficial rate of strain tensor based on velocity $\mathbf{v}_{i\alpha}$, Eq. (2.70)
$\mathbf{d}''_{i\alpha}$	microscale common curve rate of strain tensor based on velocity $\mathbf{v}_{i\alpha}$, Eq. (2.103)
$\mathbf{d}^{\overline{\overline{i\alpha}}}$	macroscale rate of strain tensor, Eq. (6.56)
$\mathbf{d}^{\overline{\overline{\alpha}}}$	macroscale rate of strain tensor, Eq. (6.64)
E	reactant species, Eq. (10.70)
E	internal energy density
$E^{\overline{\overline{i\alpha}}}$	macroscale energy of species i in entity α per total volume, Eq. (6.103)
$E^{\overline{\overline{\alpha}}}$	macroscale energy of entity α per total volume, Eq. (6.119)
$\overline{E}$	partial mass internal energy
$\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}$	partial mass energy of species i in an entity averaged over the boundary of the entity, Eq. (6.105)
$\overline{E}^{\overline{\overline{\alpha,\kappa}}}$	partial mass energy of an entity averaged over the boundary of the entity, Eq. (6.127)
$\hat{E}$	Young's modulus
$\mathbf{E}^{s}$	macroscale deformation tensor, Eq. (9.95)
$\mathbb{E}$	internal energy
$\mathcal{E}$	particular partial derivative form of a total energy conservation equation
$\mathcal{E}^{\overline{\overline{i\alpha}}}$	particular partial derivative form of a macroscale species total energy equation, Eq. (6.102) and Table 6.2
$\mathcal{E}^{\overline{\overline{\alpha}}}$	particular partial derivative form of a macroscale entity total energy conservation equation, Eq. (6.118) and Table 6.3
$\mathcal{E}_{*}$	particular material derivative form of a total energy conservation equation
$\mathcal{E}_{*}^{\overline{\overline{i\alpha}}}$	particular material derivative form of a macroscale species total energy conservation equation, Eq. (6.117) and Table 6.2
$\mathcal{E}_{*}^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity total energy conservation equation, Eq. (6.131) and Table 6.3
$\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity total energy conservation equation, Eq. (6.203)
e	internal energy per mass, Eq. (3.201)
e	energy production rate density
$e^{\overline{\overline{i\alpha}}}$	macroscale energy production rate density, Eq. (6.112)
$e_N^{\overline{\overline{wns}}}$	deviation term for the normal curvature, Eq. (8.55)
$e_G^{\overline{\overline{wns}}}$	deviation term for the geodesic curvature, Eq. (8.56)
$e^{\overline{\overline{wn}}}$	interface curvature deviation term, Eq. (8.44)

$e_J^{\overline{\overline{wn}}}$	deviation term involving curvature defined in Eq. (11.33)
$e_P^{\overline{\overline{wn}}}$	deviation term involving pressure defined in Eq. (11.34)
$e_\gamma^{\overline{\overline{wn}}}$	deviation term involving surface tension defined in Eq. (11.35)
$e_J^{\overline{\overline{\alpha s}}}$	deviation term involving curvature defined in Eq. (11.52)
$e_P^{\overline{\overline{\alpha s}}}$	deviation term involving pressure defined in Eq. (11.53)
$e_\gamma^{\overline{\overline{\alpha s}}}$	deviation term involving surface tension defined in Eq. (11.54)
$\mathbf{e}^s$	macroscale infinitesimal strain tensor
F	reactant species, Eq. (10.70)
F	scalar thermodynamic force
F	density of $\mathbb{F}$
F	tensor thermodynamic force
$\mathbf{F}$	vector thermodynamic force
$\mathscr{F}$	set of thermodynamic forces
$\mathbb{F}$	general extensive property
$\mathbb{F}$	Helmholtz potential in Chapter 3
$\mathbb{F}_T$	system functional, Eq. (4.13)
$\mathcal{F}$	partial derivative form of a general microscale conservation equation
$\mathcal{F}_*$	material derivative form of a general microscale conservation equation
f	general scalar function
$\mathbf{f}$	general tensor function
$\mathbf{f}_{kw}$	gradient of a difference in microscale potentials, Eq. (5.84)
G	gradient theorem
$\mathbb{G}$	Gibbs free energy
$\mathsf{G}_{\alpha\beta}$	microscale orientation tensor for $\alpha\beta$ interface, Eq. (8.11)
G_Ω	generation rate, Eq. (2.5)
G_{wns}	microscale orientation tensor for *wns* common curve, Eq. (8.47)
$\overset{i\kappa\to i\alpha}{G}$	general macroscale transfer associated with body force potential of species i in entity α, Eqs. (6.156) and (6.157) and Table 6.2
$\overset{\kappa\to\alpha}{G}$	macroscale transfer associated with body force potential in entity α, Eq. (6.164) and Table 6.3
$\overset{\kappa\to\alpha}{G_0}$	macroscale transfer associated with body force potential in entity α, Eq. (6.198)
$\mathcal{G}$	partial derivative form of a microscale body force potential balance equation
$\mathcal{G}^{\overline{\overline{i\alpha}}}$	particular partial derivative form of a macroscale species-based body force potential balance equation, Eq. (6.152) and Table 6.2
$\mathcal{G}^{\overline{\overline{\alpha}}}$	particular partial derivative form of a macroscale entity-based body force potential balance equation, Eq. (6.159) and Table 6.3
$\mathcal{G}_*$	particular material derivative form of a microscale body force potential balance equation
$\mathcal{G}_*^{\overline{\overline{i\alpha}}}$	particular material derivative form of a macroscale species-based body force potential balance equation, Eq. (6.158) and Table 6.2

$\mathcal{G}_*^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity-based body force potential balance equation, Eq. (6.165) and Table 6.3
$\mathcal{G}_{**}^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity-based body force potential balance equation, Eq. (6.197)
$\mathbf{g}$	body force per unit mass, acceleration
$\overline{H}$	partial mass enthalpy
$\mathbb{H}$	enthalpy
h	energy source density
$h^{\overline{\overline{i\alpha}}}$	macroscale energy source density for species i in entity α, Eq. (6.104)
$h^{\overline{\overline{\alpha}}}$	macroscale energy source density for entity α, Eq. (6.124)
$h_0^{\overline{\overline{\alpha}}}$	macroscale energy source density for entity α, Eq. (6.190)
I	unit tensor
I'	unit tensor in a surface
I''	unit tensor in a common curve
I'''	null tensor
$\mathsf{I}_\alpha^{(n)}$	unit tensor associated with $3-n$-dimensional entity, α, where (n) is the number of primes used
$\mathcal{I}$	set of entity indices
$\mathcal{I}_{\mathrm{C}}$	set of common curve indices
$\mathcal{I}_{\mathrm{c}\alpha}$	connected set of indices for entity α, $= \mathcal{I}_{\mathrm{c}\alpha}^+ \cup \mathcal{I}_{\mathrm{c}\alpha}^-$
$\mathcal{I}_{\mathrm{c}\alpha}^+$	connected set of indices of one dimension higher than entity α
$\mathcal{I}_{\mathrm{c}\alpha}^-$	connected set of indices of one dimension lower than entity α
$\mathcal{I}_{\mathrm{f}}$	set of fluid-phase indices
$\mathcal{I}_{\mathrm{I}}$	set of interface indices
$\mathcal{I}_{\mathrm{P}}$	set of phase indices
$\mathcal{I}_{\mathrm{Pt}}$	set of common point indices
$\mathcal{I}_{\mathrm{rxn}}$	set of chemical reaction indices
$\mathcal{I}_s$	set of species indices
$\mathcal{I}_{s/N}$	set of species indices except species N
$\mathcal{I}_{/S}$	set of entity indices except the solid phase, s
$\mathcal{I}_{\Gamma_\alpha}$	set of common points that bound common curve α
$\mathcal{I}_{\Omega pt}$	index set of points
i	species index
J	first curvature equal to twice the mean curvature
J	scalar thermodynamic flux
$J_\alpha^{\alpha\beta}$	macroscale average of first curvature, $\nabla'\cdot\mathbf{n}_\alpha$, over $\alpha\beta$ interface
$\mathbf{J}$	vector thermodynamic flux
J	tensor thermodynamic flux
$\mathcal{J}$	set of thermodynamic fluxes
j	jacobian
K	second curvature equal to the Gaussian curvature
$K_{Ei\alpha}$	deviation kinetic energy per mass of species i in entity α, Eq. (6.107)
$K_{Ei\alpha\kappa}$	species-based deviation kinetic energy relative to the macroscale velocity averaged over the boundary, Eq. (6.108)

$K_{E\alpha}$	deviation kinetic energy per mass of entity α, Eq. (2.35)
$K_{E\alpha\kappa}$	entity-based deviation kinetic energy relative to the macroscale velocity averaged over the boundary of the domain, Eq. (6.121)
$K_E^{\overline{\overline{i\alpha}}}$	density weighted average of $K_{Ei\alpha}$, Eq. (6.109)
$K_E^{\overline{\overline{\alpha}}}$	entity-based macroscale deviation kinetic energy, Eq. (6.120)
$K_{Ei}^{\overline{\overline{\alpha,\kappa}}}$	average of a species deviation kinetic energy over the boundary of an entity, Eq. (6.110)
$K_E^{\overline{\overline{\alpha,\kappa}}}$	average of a deviation kinetic energy over the boundary of an entity, Eq. (6.122)
$\hat{K}_M^i$	mass transfer coefficient for species i, e.g., Eq. (10.71)
$\hat{K}_E^{\alpha}$	heat transfer coefficient, e.g., Eq. (10.74)
$\hat{K}_{\mathrm{rxnk}}$	reaction rate coefficient, Eq. (5.79)
$\hat{K}_S$	bulk modulus of the solid-phase material, Eq. (9.99)
$\hat{K}_T$	bulk modulus of the solid-phase skeleton, Eq. (9.97)
$\hat{K}_w$	closure coefficient
$\hat{K}_{k\alpha}$	reaction rate coefficient, Eq. (10.69)
$\hat{\mathbf{k}}$	coefficient tensor
$\hat{k}^{wn}$	parameter for rate of relaxation of interfacial area, e.g., Eq. (8.61)
$\hat{k}_1^{wn}$	parameter for rate of relaxation of interfacial area, e.g., Eq. (11.41)
$\hat{k}^{wns}$	parameter for rate of relaxation of common curve length, Eq. (8.72)
$\hat{k}_{\theta w}$	heat conduction coefficient, Eq. (5.77)
$\hat{\mathbf{k}}_{\theta}^{\alpha}$	closure coefficient tensor for non-advective heat transfer in entity α
$\overline{L}$	partial mass common curve length
$\mathcal{L}$	set of Lagrange multipliers, Eq. (5.27)
$\mathbb{L}$	general extensive length
$\mathbf{l}$	unit vector tangent to a common curve
ℓ	length scale
ℓ_{mo}	molecular length scale, Eq. (1.1)
ℓ_{mi}	microscale length scale, Eq. (1.1)
$\ell_{\mathrm{r}}^{\mathrm{r}}$	resolution length scale, Eq. (1.1)
ℓ^{ma}	macroscale length scale, Eq. (1.1)
ℓ^{me}	megascale length scale, Eq. (1.1)
M	material derivative theorem
M_v	collection of terms in Eq. (9.36)
$\mathbb{M}$	mass
$\mathcal{M}$	set of masses of chemical species in $\mathcal{I}_s$
$\mathcal{M}_i$	set of masses of chemical species in $\mathcal{I}_s$ excluding species i
$\underset{i\kappa\to i\alpha}{M}$	microscale transfer rate of mass of species i in entity κ to species i in entity α per entity extent, Tables 2.3 and 2.4
$\overset{i\kappa\to i\alpha}{M}$	macroscale transfer rate of mass of species i in entity κ to species i in entity α per entity extent, Eq. (6.50) and Table 6.2
$\overset{\kappa\to\alpha}{M}$	macroscale transfer rate of mass of entity κ to entity α per entity extent, Eq. (6.61) and Table 6.3

$\mathcal{M}$	particular partial derivative form of a mass conservation equation
$\mathcal{M}^{\overline{\overline{i\alpha}}}$	particular partial derivative form of a macroscale species mass conservation equation, Eq. (6.48) and Table 6.2
$\mathcal{M}^{\overline{\overline{\alpha}}}$	particular partial derivative form of a macroscale mass conservation equation, Eq. (6.60) and Table 6.3
$\mathcal{M}_*$	particular material derivative form of a mass conservation equation
$\mathcal{M}_*^{\overline{\overline{i\alpha}}}$	particular material derivative form of a macroscale species mass conservation equation, Eq. (6.54) and Table 6.2
$\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$	particular material derivative form of a macroscale species mass conservation equation, Eq. (6.74)
$\mathcal{M}_*^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity mass conservation equation, Eq. (6.62) and Table 6.3
MW_i	molecular weight of species i
m	common point indicator
N	number of chemical species, or the reference chemical species
N_{rxn}	number of chemical reactions
$\mathbf{n}$	unit normal vector
$\mathbf{n}'$	unit vector normal to surface boundary and tangent to the surface
$\mathbf{n}''$	unit vector tangent to curve oriented outward at endpoints of curve
ns	interface between n and s phases
P	grand canonical potential density
P_{wn}	microscale term grouping defined in Eq. (11.26)
$P_{\alpha s}$	microscale term grouping defined in Eq. (11.48)
$\mathbb{P}$	grand canonical potential
$\boldsymbol{\mathcal{P}}$	particular partial derivative form of a momentum conservation equation
$\boldsymbol{\mathcal{P}}^{\overline{\overline{i\alpha}}}$	particular partial derivative form of a macroscale species momentum conservation equation, Eq. (6.81) and Table 6.2
$\boldsymbol{\mathcal{P}}^{\overline{\overline{\alpha}}}$	particular partial derivative form of a macroscale entity momentum conservation equation, Eq. (6.92) and Table 6.3
$\boldsymbol{\mathcal{P}}_*$	particular material derivative form of a momentum conservation equation
$\boldsymbol{\mathcal{P}}_*^{\overline{\overline{i\alpha}}}$	particular material derivative form of a macroscale species momentum conservation equation, Eq. (6.90) and Table 6.2
$\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity momentum conservation equation, Eq. (6.100) and Table 6.3
$\boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity momentum conservation equation, Eq. (6.201)
$\mathcal{P}_\alpha$	microscale property of entity α
$\mathcal{P}_i$	property i
p	pressure
p_{wn}^c	microscale capillary pressure at wn interface, Eq. (4.92)
p_T	total pressure, Eq. (9.88)
$\mathbf{p}$	momentum production rate density
$\mathbf{p}^{\overline{\overline{i\alpha}}}$	macroscale momentum production rate density, Eq. (6.80)

$\underset{j\kappa\to i\alpha}{Q}$	general microscale transfer of energy from species j in entity κ to species i in entity α, Tables 2.3 and 2.4
$\overset{j\kappa\to i\alpha}{Q}$	general macroscale transfer of energy from species j in entity κ to species i in entity α, Eqs. (6.113) and (6.115), Table 6.2
$\overset{\kappa\to\alpha}{Q}$	general macroscale transfer of energy from entity κ to entity α, Eq. (6.129), Table 6.3
$\overset{\kappa\to\alpha}{Q_0^*}$	energy exchange term between entities with dimensionality different by two, Eqs. (6.191) and (6.192)
$\overset{\kappa\to\alpha}{Q_0}$	entity-based energy exchange term that is a simple sum of species contributions, Eq. (6.193)
$\overset{\kappa\to\alpha}{Q_1}$	entity-based energy exchange term, Eq. (6.204)
$\mathbf{q}$	non-advective energy flux
$\mathbf{q}^{\overline{\overline{i\alpha}}}$	macroscale non-advective energy flux associated with species i in entity α, Eq. (6.111)
$\mathbf{q}^{\overline{\overline{\alpha}}}$	macroscale non-advective energy flux associated with entity α, Eq. (6.123)
$\mathbf{q}_0^{\overline{\overline{\alpha}}}$	non-advective energy flux for entity-based energy equation, Eq. (6.189)
$\mathbf{q}_{\mathbf{g}}^{\overline{\overline{i\alpha}}}$	non-advective energy flux associated with mechanical processes involving species i in entity α, Eq. (6.154)
$\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}$	non-advective energy flux associated with mechanical processes in entity α, Eq. (6.163)
$\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}}$	non-advective energy flux associated with mechanical processes in entity α, Eq. (6.199)
$R_{k\alpha}$	microscale molar reaction rate k in entity α
$R^{k\alpha}$	macroscale molar reaction rate k in entity α
$\hat{R}$	closure scalar
$\hat{\mathsf{R}}^{\alpha}$	closure tensor
$\hat{\mathsf{R}}^{\alpha}_{\kappa}$	closure tensor involving α and κ entities
$\mathfrak{R}$	set of mass densities of chemical species $i \in \mathfrak{I}_s$
$\mathfrak{R}_i$	set of masses of chemical species in $\mathfrak{I}_s$ excluding species i
$\mathbb{R}$	real space
r	mass production rate density
$\mathbf{r}$	microscale position vector used in Appendix B
$\mathfrak{r}$	general integration variable
$\mathbf{S}_{\Gamma}$	non-advective boundary source, Eq. (2.6)
S_{Ω}	body source independent of fluxes from adjacent entities
$S_{\Omega T}$	total body source, Eq. (2.5)
$\mathbb{S}$	entropy
$\mathcal{S}$	particular partial derivative form of an entropy balance equation
$\mathcal{S}^{\overline{\overline{i\alpha}}}$	particular partial derivative form of a macroscale species entropy balance, Eq. (6.133) and Table 6.2

$\mathcal{S}^{\overline{\overline{\alpha}}}$	particular partial derivative form of a macroscale entity entropy balance, Eq. (6.143) and Table 6.3
$\mathcal{S}_*$	particular material derivative form of an entropy balance equation
$\mathcal{S}_*^{\overline{\overline{i\alpha}}}$	particular material derivative form of a macroscale species entropy balance, Eq. (6.134) and Table 6.2
$\mathcal{S}_*^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity entropy balance, Eq. (6.144) and Table 6.3
$\mathcal{S}_{**}^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale entity entropy balance, Eq. (6.195)
s	entropy per mass, Eq. (3.201)
$s^{\overline{\overline{\alpha}}}$	saturation of fluid phase α, Eq. (6.13)
T	transport theorem
$T^{\overline{\overline{wn}}}$	collection of terms defined in Eq. (11.21)
$T^{\overline{\overline{\alpha s}}}$	collection of terms defined in Eq. (11.43)
$T^{\overline{\overline{\overline{wns}}}}$	collection of terms defined in Eq. (11.60)
$\underset{j\kappa\to i\alpha}{\mathbf{T}}$	general microscale transfer of momentum from species j in entity κ to species i in entity α, Tables 2.3 and 2.4
$\overset{j\kappa\to i\alpha}{\mathbf{T}}$	general macroscale transfer of momentum from species j in entity κ to species i in entity α, Eqs. (6.83)–(6.85) and Table 6.2
$\overset{j\kappa\to i\alpha}{\mathbf{T}^*}$	general macroscale transfer of momentum from species j in entity κ to species i in entity α where the dimensionality of the entities differs by 2
$\overset{\kappa\to\alpha}{\mathbf{T}}$	general macroscale transfer of momentum from entity κ to entity α, Eq. (6.97) and Table 6.3
$\overset{\kappa\to\alpha}{\mathbf{T}_0}$	macroscale transfer of momentum from entity κ to entity α, Eq. (6.202)
$\overset{\kappa\to\alpha}{\mathbf{T}^*}$	general macroscale transfer of momentum from entity κ to entity α where the dimensionality of the entities differs by 2, Eq. (6.98)
$\mathcal{T}_*$	particular material derivative form of an Euler equation
$\mathcal{T}_*^{\overline{\overline{i\alpha}}}$	particular material derivative form of a macroscale Euler equation for a species, Eqs. (7.44), (7.92), and (7.100) for a phase, interface, and common curve, respectively
$\mathcal{T}_*^{\overline{\overline{is}}}$	particular material derivative form of a macroscale Euler equation for a species in a solid, Eq. (7.78)
$\mathcal{T}_*^{\overline{s}}$	particular material derivative form of a macroscale Euler equation for a solid, Eq. (7.80)
$\mathcal{T}_*^{\overline{\overline{\alpha}}}$	particular material derivative form of a macroscale Euler equation for an entity, Eqs. (7.54), (7.96), and (7.102) for a phase, interface, and common curve, respectively
$\mathcal{T}_{\mathcal{G}*}$	particular form of material derivative of body source potential
$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}}$	particular macroscale form of the material derivative of the species body source potential, Eqs. (7.47), (7.95), and (7.101) for a phase, interface, and common curve, respectively

$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{is}}}$	particular macroscale form of the material derivative of the species body source potential in a solid phase, Eq. (7.79)
$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{s}}}$	particular macroscale form of the material derivative of the body source potential of a solid phase, Eq. (7.81)
$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$	particular macroscale form of the material derivative of the entity body source potential, Eqs. (7.58), (7.97), and (7.103) for a phase, interface, and common curve, respectively
t	time
$\mathbf{t}$	stress tensor
$\mathbf{t}_s$	solid-phase stress tensor, Eq. (4.25)
$\mathbf{t}_{s\mathrm{D}}$	deviatoric solid-phase stress tensor
$\mathbf{t}^{\overline{\overline{s}}}$	macroscale solid-phase stress tensor, Eq. (9.85)
$\mathbf{t}^{\overline{\overline{\alpha}}}$	macroscale stress tensor, Eq. (6.28)
$\mathbf{t}_T$	total stress tensor, Eq. (9.86)
$\mathbf{U}$	transformation function in Appendix A
$\mathcal{U}_*^{\overline{\overline{i\alpha}}}$	species-based internal energy equation, Eq. (6.206)
$\mathcal{U}_*^{\overline{\overline{\alpha}}}$	phase-based internal energy equation, Eq. (6.207)
$\mathcal{U}_{**}^{\overline{\overline{\alpha}}}$	phase-based internal energy equation, Eq. (6.209), expanded out as Eq. (6.210)
$\mathbf{u}$	diffusion/dispersion vector
$\mathbf{u}$	vector of unknown functions in Appendix A
$\mathbf{u}^{\overline{\overline{i\alpha}}}$	macroscale diffusion/dispersion vector for species i in entity α, Eq. (6.71)
$\mathbf{u}^{\overline{s}}$	macroscale displacement vector
$\mathbf{u}^{\overline{\overline{i\alpha,j\kappa}}}$	macroscale diffusion/dispersion of species i in one entity averaged over the boundary of the entity, Eq. (6.99)
$\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}$	macroscale diffusion/dispersion of a species in one entity averaged over a lower-dimensional entity, Eq. (6.130)
$\overline{V}$	partial mass volume
$\mathcal{V}$	set of variables (also with subscripts 0, M, E, F, P, I, C and Q)
$\mathbb{V}$	extensive volume
$\mathbb{V}_0$	initial extensive volume of a solid
$\mathbf{v}$	velocity
$\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}$	velocity of species i in an entity averaged over the boundary of the entity, Eq. (6.82)
$\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}$	velocity of flow in an entity averaged over the boundary of the entity, Eq. (6.96)
$\mathbf{v}^{\overline{i\alpha,j\kappa}}$	average of a species velocity in an entity over the boundary of the entity, Eq. (6.106)
W	weighting function for averaging
w	wetting phase
wn	interface between w and n phases
wns	common curve at boundary of wn, ws, and ns interfaces
ws	interface between w and s phases

$\mathbf{w}$	velocity of a domain boundary
$\mathbf{w}_{wns}$	vector velocity of normal components of *wns* common curve, Eq. (8.51)
$\mathbf{w}_{\alpha\beta}$	vector velocity of normal component of $\alpha\beta$ interface, Eq. (8.38)
X	group of exchange terms encountered in CEI derivation, Eqs. (C.33), (C.75), and (C.108)
$X_{i\alpha}$	partial mass entity extent fraction, Eqs. (3.172), (3.190), and (3.194)
$X^{\overline{\overline{i\alpha}}}$	pressure- or tension-weighted macroscale partial mass entity extent fraction, Eq. (7.7) and Eq. (7.25)
$\underset{j\kappa\to i\alpha}{X}$	general microscale transfer rate of a property from species j in entity κ to species i in entity α per entity extent
$\overset{j\kappa\to i\alpha}{X}$	general macroscale transfer rate of a property from species j in entity κ to species i in entity α per entity extent
$\mathbf{X}$	position vector in a solid in the initial state
$\mathbf{X}$	transformation function in Appendix A
$\boldsymbol{\mathsf{X}}$	tensorial partial mass volume fraction related to $\overline{\boldsymbol{\mathsf{C}}}$, Eq. (3.185)
$\boldsymbol{\mathsf{X}}^{\overline{\overline{is}}}$	tensorial macroscale partial mass volume fraction related to $\overline{\boldsymbol{\mathsf{C}}}$, Eq. (7.19)
$\mathcal{X}$	set of exchange terms in a formulation
$\mathbf{x}$	position vector
$\mathbf{x}$	vector of independent variables in Appendix A
$\mathbf{x}^*$	functional relation between $\mathbf{x}$ and $\mathbf{X}$
$\underset{j\kappa\to i\alpha}{z_Q}$	microscale exchange coefficient for energy, Eq. (2.80)
$\underset{j\kappa\to i\alpha}{z_T}$	microscale exchange coefficient for momentum, Eq. (2.75)
$\underset{j\kappa\to i\alpha}{z_\Phi}$	microscale exchange coefficient for entropy

Greek Symbols

α	entity index
$\hat{\alpha}$	isobaric thermal expansion coefficient
$\hat{\alpha}_B$	Biot coefficient, Eq. (9.92)
$\hat{\alpha}_{\mathrm{Bs}}$	bulk compressibility of the solid, Eq. (9.112)
β	entity index
$\hat{\beta}$	isothermal compressibility
$\hat{\beta}_w$	w phase compressibility, Eq. (9.113)
$\hat{\beta}_s$	s phase compressibility, Eq. (9.114)
Γ	boundary of a domain
Γ_{C_m}	set of points that bound the curves in Ω_C
Γ_{vv}	portion of boundary of Ω_v intersecting Ω_V
Γ_v	portion of boundary of Ω_v coincident with boundary of Ω_V
γ	interfacial or surface tension; common curve lineal tension
γ	entity index

δ	Dirac delta
δ	first-order variation
δ_{ij}	Kronecker delta
$\overline{\delta}$	fixed-point variation
$\overline{\delta}'$	fixed-point variation on a surface, Eq. (A.61)
$\overline{\delta}''$	fixed-point variation on a common curve, Eq. (A.78)
$\overline{\delta}^{(n)}$	fixed-point variation on an entity of dimension $3-n$
ε	porosity
ε	small parameter in Appendix A
$\varepsilon^{\overline{\overline{\alpha}}}$	specific entity measure, Eq. (6.9)
η	entropy density
$\overline{\eta}$	partial mass entropy
$\eta^{\overline{\overline{i\alpha}}}$	macroscale entropy of species i in entity α per volume, Eq. (6.135)
$\eta^{\overline{\overline{\alpha}}}$	macroscale entropy of entity α per volume, Eq. (6.145)
$\overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}}$	macroscale partial mass entropy of species i per volume in an entity averaged over the boundary of the entity, Eq. (6.137)
$\overline{\eta}^{\overline{\overline{\alpha,\kappa}}}$	macroscale sum of weighted partial mass entropy per volume in an entity averaged over the boundary of the entity, Eq. (6.147)
θ	temperature
$\theta^{\overline{\overline{i\alpha}}}$	species entropy weighted macroscale temperature of species i in entity α, Eq. (7.5)
$\theta^{\overline{\overline{\alpha}}}$	entropy weighted macroscale temperature of entity α, Eq. (7.15)
$\theta_\alpha^{\overline{\overline{\alpha\beta}}}$	entropy-weighted average of microscale temperature θ_α over entity $\alpha\beta$, Eqs. (7.108) and (7.109)
κ	entity index
κ_{Gwns}	microscale geodesic curvature, Eq. (4.86)
κ_{Nwns}	microscale normal curvature, Eq. (4.85)
$\hat{\kappa}$	bulk viscosity
Λ	entropy production rate
$\Lambda^{\overline{\overline{i\alpha}}}$	macroscale entropy production rate associated with species i in entity α, Eq. (6.138)
$\Lambda^{\overline{\overline{\alpha}}}$	macroscale entropy production rate associated with entity α, Eq. (6.149)
λ	real positive scaling multiplier employed in Chapter 3
λ	Lagrange multiplier
$\lambda_{\mathcal{E}}^{i\alpha}$	Lagrange multiplier for energy conservation equation of species i in entity α
$\lambda_{\mathcal{G}}^{i\alpha}$	Lagrange multiplier for potential energy balance of species i in entity α
$\lambda_{\mathcal{M}}^{i\alpha}$	Lagrange multiplier for mass conservation equation of species i in entity α
$\lambda_{\mathcal{T}}^{i\alpha}$	Lagrange multiplier for thermodynamic equation of species i in entity α
$\lambda_{\mathcal{T}\mathcal{G}}^{i\alpha}$	Lagrange multiplier for derivative of potential energy of species i in entity α

$\lambda_{\mathbb{M}_\alpha}$	constant multiplier, Eq. (4.13)
$\lambda_{\mathbb{S}}$	constant multiplier, Eq. (4.13)
$\boldsymbol{\lambda}$	vector Lagrange multiplier
$\boldsymbol{\lambda}_{\mathcal{P}}^{i\alpha}$	Lagrange multiplier for momentum conservation equation of species i in entity α
μ	chemical potential
$\hat{\mu}$	dynamic viscosity
ν_{ik}	stoichiometric coefficient for component i in reaction k
$\hat{\nu}$	Poisson's ratio
$\boldsymbol{\xi}$	microscale coordinate system with origin at centroid of an REV
ρ	mass density
$\boldsymbol{\sigma}$	solid-phase stress tensor, Eq. (3.135)
$\boldsymbol{\sigma}^{\overline{\overline{s}}}$	macroscale solid-phase stress tensor, Eq. (7.18)
τ	dissipative part of the stress tensor
τ_{g}	general time scale
τ_{t}	thermodynamic time scale
$\boldsymbol{\tau}^{\overline{\overline{s}}}$	factor of effective stress tensor, $\varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}}$
Υ_C	curve indicator function, Eq. (B.47)
Υ_S	surface indicator function, Eq. (B.18)
Υ_V	volume indicator function, Eq. (B.4)
Υ_α	indicator function for entity α, Eq. (A.33)
$\underset{j\kappa\to i\alpha}{\Phi}$	general microscale transfer of entropy from species j in entity κ to species i in entity α, Tables 2.3 and 2.4
$\overset{j\kappa\to i\alpha}{\Phi}$	general macroscale transfer of entropy from species j in entity κ to species i in entity α, Eqs. (6.139) and (6.141) and Table 6.2
$\overset{\kappa\to\alpha}{\Phi}$	general macroscale transfer of entropy from entity κ to entity α, Eq. (6.150) and Table 6.3
$\overset{\kappa\to\alpha}{\Phi}_0$	entity-based entropy exchange term that is a simple sum of species contributions, Eq. (6.196)
$\varphi_{ws,wn}$	microscale contact angle between ws and wn interfaces
$\varphi^{\overline{\overline{ws,wn}}}$	macroscale measure of contact angle, Eqs. (8.65) and (8.66)
$\boldsymbol{\varphi}$	non-advective entropy flux
$\boldsymbol{\varphi}^{\overline{\overline{i\alpha}}}$	macroscale non-advective entropy flux associated with species i in entity α, Eq. (6.136)
$\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}$	macroscale non-advective entropy flux associated with entity α, Eq. (6.148)
χ	entity index
$\chi_\alpha^{\overline{\overline{\kappa}}}$	fraction of boundary of entity α in contact with entity κ, Eq. (8.23)
Ψ	body force potential density
$\Psi^{\overline{\overline{i\alpha}}}$	species-based macroscale body force potential density, Eq. (6.153)
$\Psi^{\overline{\overline{\alpha}}}$	entity-based macroscale body force potential density, Eq. (6.161)
ψ	body force potential per unit mass

$\psi^{\overline{\overline{\alpha,\kappa}}}$	macroscale average of body force potential density associated with one entity averaged over a lower-dimensional entity, Eq. (6.162)
$\psi_i^{\overline{\overline{\alpha,\kappa}}}$	macroscale average of body force potential density associated with species i in one entity averaged over a lower-dimensional entity, Eq. (6.155)
Ω	domain
Ω_C	curve within global domain of interest
$\Omega_{C\infty}$	extended curve domain
Ω_{PT}	set of points within global domain of interest
Ω_S	surface within global domain of interest
Ω_{S_Ω}	extended surface integration region
$\Omega_{S\infty}$	extended surface domain
Ω_V	a three-dimensional domain subset of the global domain
Ω_c	subdomain of Ω_C within averaging region
Ω_{pt}	subdomain of Ω_{PT} within averaging region
Ω_s	subdomain of Ω_S within averaging region
Ω_{s0}	undeformed solid-phase domain
Ω_v	subdomain of Ω_V
Ω_∞	global domain encompassing all of space
$\bar{\Omega}$	domain including its boundary
ω	mass fraction
$\omega_i^{\overline{\overline{\alpha,\kappa}}}$	mass fraction of an entity averaged over the boundary of the entity, Eq. (6.128)

Superscripts

i	chemical species qualifier
k	chemical species qualifier
n	macroscale non-wetting phase qualifier
ns	macroscale qualifier for interface between n and s phases
ss	total surface of solid-phase qualifier
s	macroscale solid-phase qualifier
T	transpose
w	macroscale wetting-phase qualifier
wn	macroscale qualifier for interface between w and n phases
wns	macroscale qualifier for common curve where wn, ws and ns interfaces meet
ws	macroscale qualifier for interface between w and s phases
α	macroscale entity qualifier
α	intrinsic average over entity α or macroscale property of entity α
$\overline{\alpha}$	mass average over entity α
$\overline{\overline{\alpha}}$	uniquely defined average over α
$*$	indicates a concentrated force in an exchange between entities with a difference in dimensionality greater than 1

$*$	indicates a functional form of a thermodynamic property, primarily used in Chapter 3
$*$	transformed quantity in Appendix A
$^{-}$	above a superscript refers to a density weighted macroscale average
$^{=}$	above a superscript refers to a uniquely defined macroscale average with the definition provided in the text
$'$	vector tangent to a surface
$''$	vector tangent to a common curve

Subscripts

$\mathcal{E}$	associated with the total energy conservation equation
$\mathbb{E}^*$	equation of state based on internal energy variables
eq	equilibrium
$\mathbb{F}^*$	equation of state based on Helmholtz free energy variables
$\mathbb{G}^*$	equation of state based on Gibbs free energy variables
$\mathcal{G}$	associated with the potential energy equation
g	microscale gas-phase qualifier
$\mathbb{H}^*$	equation of state based on enthalpy variables
i	chemical species qualifier
k	chemical species qualifier
k	chemical reaction identifier
$\mathcal{M}$	associated with the mass conservation equation
n	microscale non-wetting-phase qualifier
ns	microscale qualifier for interface between n and s phases
$\mathcal{P}$	associated with the momentum conservation equation
s	microscale solid-phase qualifier
ss	refers to the total boundary of the s phase
T	total
$\mathcal{T}$	associated with the thermodynamic equation
$\mathcal{T}_{\mathcal{G}}$	associated with the derivative of potential energy equation
V	volume
v	volume
w	microscale wetting-phase qualifier
wn	microscale qualifier for interface between w and n phases
wns	microscale qualifier for common curve where wn, ws and ns interfaces meet
ws	microscale qualifier for interface between w and s phases
α	microscale entity qualifier
$\alpha\alpha$	refers to the total boundary of entity α

Other Mathematical Symbols

$\mathrm{D}_{i\alpha}/\mathrm{D}t$	material derivative with microscale velocity $\mathbf{v}_{i\alpha}$, Eqs. (2.15), (2.69), (2.102), (2.115)
$\mathrm{D}^{\overline{i\alpha}}/\mathrm{D}t$	material derivative with macroscale velocity $\mathbf{v}^{\overline{i\alpha}}$, Eqs. (6.55) and (7.36)
$\mathrm{D}^{\prime\overline{s}}/\mathrm{D}t$	material derivative on a surface where the macroscale solid is employed, Eq. (7.84)
$\mathrm{D}^{\prime\prime\overline{s}}/\mathrm{D}t$	material derivative on a curve where the macroscale solid is employed, Eq. (7.98)
$\partial'/\partial t$	partial time derivative at a point fixed on a surface, Eq. (2.55)
$\partial''/\partial t$	partial time derivative at a point fixed on a common curve, Eq. (2.91)
$\partial'''/\partial t$	partial time derivative fixed to a common point, Eq. (2.115)
$\partial^{(n)}/\partial t$	partial time derivative at a point fixed on $3-n$-dimensional entity, (n) is replaced by n primes
∇'	microscale surficial del operator, Eqs. (2.57) and (B.20)
∇''	microscale common curve del operator, Eqs. (2.93) and (B.49)
∇'''	microscale common curve del operator, Eq. (B.72)
$\nabla^{(n)}$	microscale del operator for a $3-n$-dimensional entity where (n) is the number of primes
∇_X	gradient operator with respect to $\mathbf{X}$ coordinates
$\nabla_{\mathbf{x}}$	gradient operator with respect to macroscale $\mathbf{x}$ coordinates
$\nabla_{\boldsymbol{\xi}}$	gradient operator with respect to microscale $\boldsymbol{\xi}$ coordinates
div	divergence operator, Eq. (2.10)
div′	surface divergence operator, Eq. (2.58)
div″	common curve divergence operator, Eq. (2.94)
(n)	denotes the number of primes that should appear
$\hat{}$	a parameter defined at the scale indicated by the subscript or superscript on the parameter
$\langle f_\alpha\rangle_{\Omega_\beta,\Omega_\gamma,W}$	$= \left(\int\limits_{\Omega_\beta} W f_\alpha \,\mathrm{d}\mathfrak{r}\right)/\left(\int\limits_{\Omega_\gamma} W \,\mathrm{d}\mathfrak{r}\right)$, general average of microscale property f_α, Eq. (6.1)
f_α^β	$= \langle f_\alpha\rangle_{\Omega_\beta,\Omega_\beta}$, Eq. (6.2)
f^α	$= \langle f_\alpha\rangle_{\Omega_\alpha,\Omega_\alpha}$, intrinsic average, Eq. (6.3)
$f_\alpha^{\overline{\beta}}$	$= \langle f_\alpha\rangle_{\Omega_\beta,\Omega_\beta,\rho_\alpha}$, general density-weighted average, Eq. (6.4)
$f^{\overline{\alpha}}$	$= \langle f_\alpha\rangle_{\Omega_\alpha,\Omega_\alpha,\rho_\alpha}$, intrinsic density-weighted average, Eq. (6.5)
$f_{i\alpha}^{\overline{\beta}}$	$= \langle f_{i\alpha}\rangle_{\Omega_\beta,\Omega_\beta,\rho_\alpha\omega_{i\alpha}}$, general species mass density weighted average, Eq. (6.6)
$f^{\overline{i\alpha}}$	$= \langle f_{i\alpha}\rangle_{\Omega_\alpha,\Omega_\alpha,\rho_\alpha\omega_{i\alpha}}$, intrinsic species mass density weighted average, Eq. (6.7)
tr	trace

Abbreviations

AEI	augmented entropy inequality
CEI	constrained entropy inequality
CIT	classical irreversible thermodynamics
EI	entropy inequality
EPFL	École Polytechnique Fédérale de Lausanne
EPP	entropy production postulate
REV	representative elementary volume
SEI	simplified entropy inequality
TCAT	thermodynamically constrained averaging theory
TCM	thermodynamically consistent modeling
UNC	University of North Carolina

Chapter 1
Elements of Thermodynamically Constrained Averaging Theory

1.1 Overview

Mechanistic computational modeling of environmental systems presupposes the existence of a properly posed set of equations that adequately describes the underlying physical, chemical, and biological processes at time and length scales consistent with the problem being addressed. Efforts to improve the user interface, computational accuracy, or computational efficiency of a model will be fruitless if these improvements are applied to a fundamentally inappropriate system description. Nevertheless, it seems fair to assert that far more effort has been employed in improving the computational solution of a set of system-descriptive differential equations than in improving the fidelity of mechanistic models represented by the equations themselves. Perhaps this is because visually appealing graphs of system performance lend themselves more readily to dissemination among decision makers and generalists than do highly symbolized, superscripted, subscripted, multi-alphabetical equations that by themselves do not display system performance. Indeed, these equations are a way station between qualitative system descriptions and the appealing plots and graphs whose quantitative accuracy seems somehow proportional to the number of colors used and the awe-inspiring elements of the animation of those colors. The "way station" tends to get lost between the recognition of an interesting problem and the predicted evolution of system behavior or solution of the problem.

The scope and scale of environmental problems are virtually unlimited. They span processes encompassing molecular interactions, microbial community growth, subsurface flow in soils, sands, and fractures, riverine and estuarine flow and transport, watershed hydrology, ocean flows and temperature oscillations, formation of hurricanes and tornadoes, and global climate change. Additionally processes related to extraterrestrial elements and stresses such as tide generating forces and solar storms can have enormous environmental impacts. Although all of these processes are governed by a single set of natural laws, an attempt to model them using a single equation framework would be unworkable. The present document is concerned with modeling of flows in the subsurface or, more generally, in porous media. The

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objective is to develop sets of equations appropriate for modeling properties of and fluxes in porous medium systems.

Porous medium systems are defined to include a continuous solid skeleton and a connected pore space that allows one or more fluids to flow though it. Though the solid may deform, this movement, relative to that of the fluids, is usually small. With the solid phase presumed present, porous media flow is commonly referred to as single phase, or two phase, or multiphase depending on the number of immiscible fluid phases involved. This description is important because of the significant differences in physics and complexity that exist among these classes of applications. Porous medium problems can also involve changes in the composition of phases due to species transport within a phase and between immiscible phases, as well as due to chemical or biological reactions. In addition, porous medium systems may be at a relatively constant temperature or may undergo significant changes in temperature. The number of phases, composition, thermal characteristics, and length and time scales of processes in porous media lead combinatorially to a large number of specific types of systems of relevance and interest.

Processes that occur routinely in natural, engineered, and organismic porous medium systems can be described mechanistically using the fundamental equations of mass, momentum, and energy conservation. The development of mathematical models based on these equations that describe the processes at an appropriate scale is an important scientific pursuit. While models are sometimes touted merely for their predictive ability, in fact their utility lies most importantly in providing a systematic framework for studying processes, in determining which processes are being modeled in a physically meaningful manner, and in identifying where data support is needed. Ultimately, the ability of a model to describe the behavior of a porous medium system of interest is a direct measure of the level of comprehensive scientific understanding of that system.

The length scale of many porous medium applications is large compared to the length scale of solid-phase features that comprise the skeleton of the system, such as the grain diameter or the effective diameter of a flow channel. For these applications, it is impossible to define the morphology and topology of the pore structure, including the location of the solid surfaces, over the full domain of interest. For example, Fig. 1.1 is an image of a fabricated two-dimensional micromodel that is 600 microns on each side. This small region has been digitized using 10^6 pixels. Describing a region like this in three dimensions would require 10^9 pixels. It should be clear that besides the challenge of accessing a subsurface system for this degree of characterization without destroying it, digitization of a region with a size on the order of meters or larger would be infeasible. On top of this, efforts to describe the movement of fluids, their properties, and their evolving interfaces in the multifluid case would require layers of detail and data that are unthinkable to manage. On the other hand, the mechanistic equations that describe the behavior of an individual phase are well known only at the small scale. Thus, if a system under consideration is to be described in a way that the flow paths and solid phase are accounted for in an average sense and with a low-dimensional parameterization, it is necessary also to average or upscale the defining equations to this more practical and useful

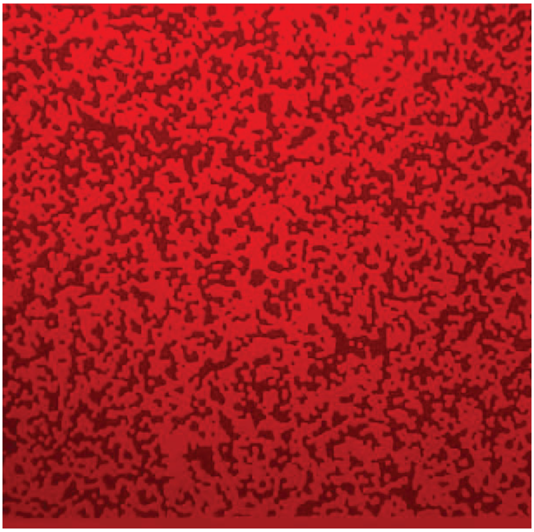

Fig. 1.1 Two-dimension micromodel with dimensions of 600 × 600 microns. Darker region is the solid with lighter region the pore space [22]

scale. One method for achieving this change in equation scale is the *thermodynamically constrained averaging theory* (TCAT). This approach can be employed to perform consistent and rigorous upscaling of conservation, balance, and thermodynamic equations. TCAT ensures that all approximations will be encountered explicitly such that resultant larger-scale models are consistent with smaller-scale variable definitions and conventions. Therefore, modifications and extensions to equations can be achieved systematically to incorporate needed degrees of detail.

The purpose of this chapter is to discuss the elements of the TCAT approach, as well as the role of each element in the total formulation of the description of a problem of interest. This chapter does not provide mathematical details but is intended to provide a qualitative explanation and overview of TCAT. In essence, TCAT is a rigorous procedure based on conservation and thermodynamic principles for producing consistent system models at a scale or scales of interest. Implementation of the TCAT approach leads to models that describe many features and attributes at the larger scale not typically identified using heuristic or other mathematical approaches. Included among these features are:

- consideration of important physical phenomena (e.g., interface reorganization and orientation, driving forces for various fluxes);
- precise and consistent definitions of larger-scale variables in terms of microscale precursors;

- a hierarchy of sophistication in accounting for phenomena that influence system behavior (e.g., interphase dynamics, chemical species transport, multiphase flow) such that fidelity to observations can be achieved; and
- identification of experimental and computational approaches for evaluating the quality of resultant models and refining them within the TCAT structure.

The rigor and consistency inherent in TCAT require detailed mathematical manipulations. The steps involved in TCAT analysis can be compartmentalized, and the relations among the steps described concretely. This conceptual approach is employed subsequently in giving an overview of the TCAT approach. Mathematical details are left to subsequent chapters. While the mathematical steps are extensive and can be tedious, the TCAT framework itself is not difficult to describe. Thus, the reader is encouraged to focus, at least at first, on an overview of the elements of the method which provides motivation to dig into the mathematical manipulations. Otherwise, a direct excursion into the mathematics without appreciating the elements of TCAT can be frustrating, confusing, and off-putting. Perhaps more importantly, an understanding of the TCAT approach and philosophy makes the differences between this method and other methods clearer so that one can discern TCAT's particular attractive attributes. Because some of the elements of TCAT involve direct application of mathematical relations, these need to be performed only once to provide a "jumping in" point for subsequent TCAT analysis. By gaining an understanding of TCAT, including appreciation of the parts that can be employed directly as well as those that require insight, finesse, or approximation, the potential user can more efficiently investigate systems of interest and their unique features.

1.2 Identification of Scales for Modeling

Prior to laying out the features of TCAT, we first consider length scales and time scales. Because TCAT is a method that facilitates increasing the length scale at which a problem is examined, it is important to first understand some of the issues related to scale that are inherent in the method. It is useful to recognize that dealing with scale is one of the great challenges in successfully formulating a myriad of problems. Indeed references are made to the "tyranny of scale" in a wide range of disciplines [9, 96, 110]. Here we discuss a framework for identifying various length and time scales.

1.2.1 Length Scales

Porous medium systems can span length scales that range from millimeters to hundreds of kilometers in processes including energy generation in hydrogen fuel cells, geologic carbon storage, petroleum recovery, waste remediation, oxygen transport in lungs, and water supply. In deciding what processes are to be considered and understood in a system of interest, the issue of the scale at which the processes will be studied is important. For example, in considering contamination of an aquifer as a whole, the length scale of the system might be deemed to be relatively large. However, if one is interested in growth of a microbial community at some location in the aquifer, the length scale could be very small. Identification of the length scale is related to the detail with which features of the system and of processes in the system are to be described. Not only is the magnitude of the length scale of the system of importance, but so also is the length scale of the features that describe the pore morphology and topology when modeling porous medium systems. Models may be developed at length scales where the pore structure is precisely defined such that the location of individual fluid-phase boundaries within the pore structure are resolved accurately [e.g., 16, 20, 22, 33, 90, 94, 122]. Alternatively, models may be defined in which the details of pore structure are not resolved and are instead treated in an averaged sense [e.g., 18, 31, 73, 82, 91, 92]. Lastly, models may be derived in which all of the details of pore structure within the system in one or more spatial dimensions are neglected by averaging over the entire length of the system in those dimensions. Models of this type are used, for example, to assess the total amount of water stored in an aquifer or the overall fluxes of nutrients and water into a region [e.g., 3, 51]. This progression of models leads to representations with a range of fidelity, with the appropriate representation dependent upon the questions being investigated in the application.

Besides the inherent issue of defining length scales, the issue of separation of those scales is important. Separation of scales means that one scale of observation is separated from another by orders of magnitude. This quality carries with it the property that variation in measurements is negligible with respect to changes in the length scale of that measurement unless the length scale changes by several orders of magnitude. This qualification is important because if the length scales are not separated, collection of data will be strongly dependent on the scale employed. For example, a measurement of the density of water at a particular location in an aquifer will yield the same result whether it is based on a cubic centimeter or a liter of water. The size of the measuring instrument, from a thimble to a bucket, does not impact the value of density obtained in this instance. One can imagine that a measurement of density obtained by collecting only several water molecules or by considering all the water in a geothermal aquifer with high variability of temperature could yield a result quite different from a measurement taken with a measuring device that collects samples with a size on the order of a few centimeters. If the length scale were important in measuring the density of water, all values reported in the literature would have to be accompanied by an explicit mention of the length scale of the measuring device. Fortunately, this is usually not the case in measuring density as invariant measures may be obtained over a wide range of sampling length scales. Length scale considerations are also important for measuring other properties of interest such as temperature, pressure, velocity, and chemical concentration. When gradients of a property of interest are large, the average value of that property can be strongly dependent on the length scale of the measurement. Conversely the calculated gradient of a property can be strongly influenced by the length scale employed in measuring the property.

We will be considering cases where the length scales are widely separated such that variables and parameters that appear in the equations can be considered to be scale invariant (at least over a couple of orders of magnitude). This idealization introduces the concept of a hierarchy of length scales. Thus, in working with specific applications, we will not include explicit quantification of the length scale but will only qualitatively categorize the scale of interest. We emphasize, however, that the concept of "scale invariance" as employed here should not be understood to indicate that an equation derived at a particular scale can be applied at any scale. Scale invariance only means that, within a couple of orders of magnitude of length, the equations, variables, and parameters need not be adjusted. This will become clearer if we present the qualities of the various length scales of interest as they will be employed here.

For the purposes of this text, we will identify five different, separated length scales that satisfy the conditions

$$\ell_{\mathrm{mo}} \ll \ell_{\mathrm{mi}} \ll \ell_{\mathrm{r}}^{\mathrm{r}} \ll \ell^{\mathrm{ma}} \ll \ell^{\mathrm{me}} \, . \tag{1.1}$$

These scales, from smallest to largest, are referred to, respectively, as the molecular scale, the microscale, the resolution scale, the macroscale, and the megascale. Although the actual magnitudes of these scales will vary from system to system and are, in fact, not associated with a specific length that is universally applicable, this qualification of scales is useful for discussion of systems.[1] The fact that the scales are widely separated in length is as important to their definition as are their actual sizes for purposes of facilitating subsequent discussion. Unfortunately, despite the stipulation of a clear discrete set of separated length scales proposed here, many natural porous medium systems actually consist of a hierarchy of many different length scales that may or may not have a clear separation [25]. While such systems occur routinely and are important, these systems are outside the scope of our current focus. In a more general exposition, the TCAT approach can be employed, admittedly with significant additional effort to account explicitly for length scale factors, for the study of systems without a clear separation of length scales.[2] For convenience, a schematic of the five length scales is provided in Fig. 1.2.

The molecular scale, ℓ_{mo}, is identified as the mean free path for molecular collisions within a phase in a system of interest, the average distance that a molecule

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[1] The terminology employed here is not universal. For example, what we refer to as the "microscale" is commonly called the "macroscale" in thermodynamic vernacular. Thus one must exercise caution in using these terms.

[2] In scientific inquiry, it is always convenient and even comforting to have a precise set of definitions from which to work. We note that the study of porous media tends to deny such comfort. The distinction between a mixture of solids and fluids vs. a porous medium system is imprecise; immiscibility of fluid phases is not complete; the definition of length scales is fraught with caveats. It is important to understand that the definitions are nevertheless made to provide an opportunity to move forward while also acknowledging that the lack of precise definitions impacts one's ability to describe porous medium processes.

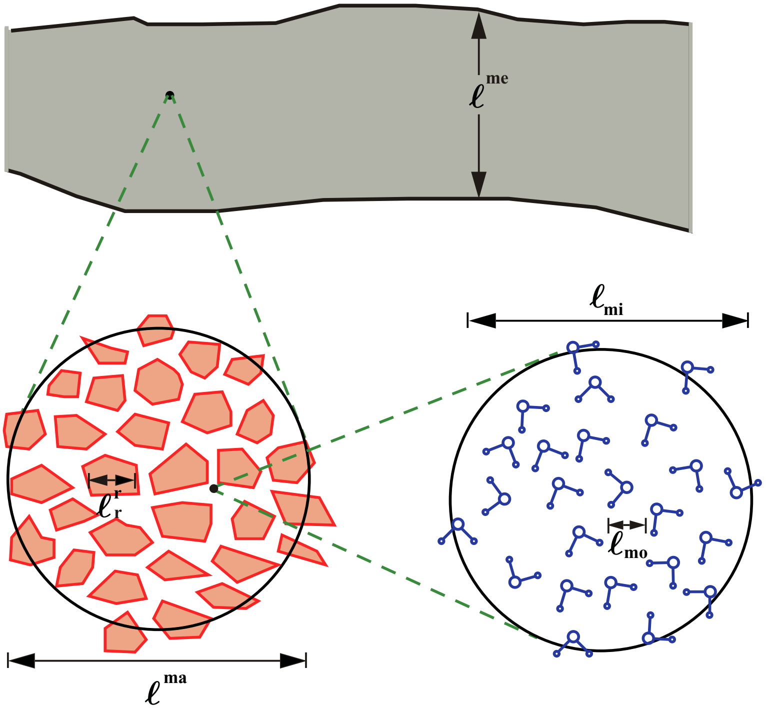

Fig. 1.2 Schematic of the five length scale of importance (not to scale) with regard to a porous medium system. An aquifer appears at the top. A small portion of the porous medium is at the bottom left with the solid grains in red and fluid filling the space between the grains. At the bottom right is a small sample of fluid that is composed of molecules. Measures of the molecular scale (ℓ_{mo}), microscale (ℓ_{mi}), resolution scale ($\ell_{\mathrm{r}}^{\mathrm{r}}$), macroscale ($\ell^{\mathrm{ma}}$), and megascale ($\ell^{\mathrm{me}}$) are indicated

travels between collisions with other molecules. For a gas, the larger the molecules and the higher the density, the smaller the mean free path. For O_2 at standard conditions of pressure (1 bar) and temperature (25°C), ℓ_{mo} is approximately 7×10^{-8} m. For a liquid, the collision scale is roughly the diameter of the molecule. The diameter of a water molecule is approximately 3×10^{-10} m. For solids, in which the positions of molecules relative to each other are approximately fixed, a quantity called the inelastic mean free path is employed. This length is the distance an electron beam will travel through a solid before its intensity decays to e^{-1} of its initial value. At the molecular scale, a system would have to be modeled as a discrete system in terms of the molecules, their velocities, and their collisions. Molecular dynamic models provide insight into chemical reactions of importance, but at too small a scale to be able to model a porous medium.

Almost all of the attention here is focused on scales larger than the molecular scale. The microscale, ℓ_{mi}, is often referred to in the porous medium literature as the pore scale. It is a scale at which all the phases, interfaces, and common curves are resolved such that both the distribution of phases within the system and also boundaries between the phases are identifiable. At the microscale, a phase behaves as a continuum, rather than as a collection of discrete molecules. A continuum approximation neglects the fact the material is made of individual molecules but rather envisions the space as being completely occupied by a substance that fills the space. Continuum properties, such as mass density or momentum density, can be obtained as averages of molecular scale properties over a region with a microscale length scale. The formulation of physical laws used to describe a system at the microscale makes use of the fact that the phases behave as continua with smooth variation of properties such that principles of mass, momentum, and energy conservation may be applied. Additionally, fully-dynamic, microscale, continuum conservation equations that describe interfacial and common curve processes in two and one spatial dimension, respectively, may be formulated. An example of the microscale perspective is the description of the flow of water in a saturated porous medium where individual solid particles are described and resolved. The particle surfaces are treated as boundaries of the fluid phase such that the gradients in fluid velocity in the space between particles can be described continuously. At the microscale, phases are seen to be next to each other with identifiable boundaries and distributions of material within the system. Additionally, the quantities appearing in microscale continuum equations involve a length scale large enough that measurements of these properties are stable with respect to perturbations in the size of the measurement instrument. A minimum length scale for such an average is typically an order of magnitude larger than the molecular interaction scale. Thus, for O_2 under standard conditions of temperature and pressure, ℓ_{mi} is larger than 10^{-6} m (1 μm), while ℓ_{mi} for a liquid microscale is roughly 2.5 orders of magnitude smaller than this. For a system in which the gradient of a property being measured is zero, and remains zero as the length scale of the sampling volume increases, the measurement of that property will be unchanged as the microscale increases orders of magnitude above its minimum value. Thus, the minimum ℓ_{mi} is related to some multiple of mean free path while the maximum value of ℓ_{mi} is related to the scale of any heterogeneities in the system. Even though the minimum values of ℓ_{mi} are different for a gas, liquid and solid, modeling of a gas-liquid-solid porous medium system at the microscale is usually accomplished when a common value of ℓ_{mi} is implicitly assumed to be applicable to all phases.

The resolution scale, $\ell_{\mathrm{r}}^{\mathrm{r}}$, is the length scale needed to resolve internal features related to transport phenomena for a system of concern. The resolution scale is particularly important for porous media as it relates to the natural length scales of the system. For a natural system, the average diameter of a sand grain is typically on the order of 10^2 μm. If the grains are well sorted, such that all are approximately of the same size, this would be the resolution scale. However, granular porous systems may contain solid particles ranging in size from approximately 1 μm to 10^{-1} m or larger. The features of a general porous system may include small pores, fractures that are evident on a larger scale, boulders, and, perhaps, caves formed by a karstification process. Thus, although the molecular scale and the microscale can be defined within a relatively easily reasoned length, identification of the resolution scale is complicated by the features one wishes to study and the distribution of the characteristic lengths that describe those features. The resolution scale will vary widely depending on the problem of interest.

The macroscale, ℓ^{ma}, is a scale at which each entity of the porous medium—phase, interface, or common curve—can be treated as a continuum in the full space of the porous medium. Thus at the macroscale, the porous medium system is modeled as being composed of overlapping continua, simultaneously present at each macroscale point. At this scale, the detailed microscale distribution of the locations of adjacent phases is not resolved but is accounted for in an average sense. Phases are described merely as occupying fractions of available space, and the interfacial areas per volume between phases and common curve lengths per volume are considered. These densities, as well as porosity, the fraction of space not occupied by solid phase, do not exist at the microscale but arise as a consequence of averaging.[3] Descriptions of the system are expressed in terms of macroscale properties that are averages of microscale properties over regions of a size characterized by the macroscale length scale, ℓ^{ma}. For example, a macroscale velocity of a fluid phase is an average of the microscale velocity of that phase within the pore space contained in the macroscale volume.

The stipulation of separation of scales provides the condition that the value of the macroscale average is insensitive to variations in the size of the averaging volume. Satisfaction of this stipulation, in practice, requires the macroscale to be larger than the resolution scale such that it incorporates a representative region of the porous medium. At a minimum, ℓ^{ma} should be at least 10 times the resolution scale. More stable values of porosity and other macroscale variables are typically obtained when ℓ^{ma} is on the order of 10^2 times the resolution scale. For a well-sorted sample with grain sizes on the order of 10^2 μm, these considerations result in a macroscale of approximately 10^{-2} m. However, depending upon how the fluids are distributed within the porous medium system, the macroscopic length scale might have to be increased to obtain stable values of interfacial areas per volume [77].

Within the mathematical framework to be developed here, the implicit assumption is made that all macroscale variables may be specified at the same length scale, regardless of the phase, interface, or common curve being modeled. This constraint most certainly raises concerns about the stability of all macroscale quantities with respect to changes in length scale. Additionally, in some systems there will be more than one identifiable macroscopic length scale. For example, in a system composed of a fractured porous medium, one macroscale may be employed relative to the pore diameter or grain size while a larger macroscale can be identified relative to the fractures. Modeling of the whole system requires that techniques be employed that couple these two domains.

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[3] The creation of new parameters or variables that characterize a system is a common feature of increasing scale size. At the microscale, for example, pressure, density, and temperature arise while they do not exist at the molecular scale where molecular velocities and collisions describe the system.

The macroscale has also been referred to as the "Darcy scale". This is a somewhat misleading designation. At the macroscale, one models the spatial variability of the quantities of interest. The conservation equations make use of terms involving time and space derivatives. The use of the "Darcy" designation for this scale honors fine experimental work that was conducted in the mid 19th century [11, 26, 27]. However, the work of Darcy consisted of column experiments performed to describe the behavior of a system consisting of sand and a fluid as a single unit without measurement of variability within the column. The total flow through the column was measured as a function of the boundary conditions imposed at each end of the column. Thus, Darcy's experiments were not actually concerned with macroscale properties, despite the fact that these properties are confusingly referred to as "Darcy scale" properties. Darcy was concerned with system behavior at a larger scale.

The megascale, ℓ^{me}, is the length scale of the domain of the system of interest. Note that a domain may have different megascopic length scales in different directions. For example, a groundwater aquifer may extend for kilometers in the lateral direction while being only a few meters thick in the vertical direction. The megascale must be much larger than ℓ^{ma} because macroscale quantities may be defined only at points farther than $\ell^{\mathrm{ma}}/2$ from the boundary of the domain. Therefore, if variations in properties and gradients of variables are to be defined meaningfully in most of the domain, ℓ^{me} must be much larger than ℓ^{ma}. Note that in some cases, it is useful to average from the microscale over a full system dimension corresponding to a megascale representation in that dimension. When averaging occurs over a dimension, no variation of properties in that dimension is considered in the final equations developed. For example, in modeling nearly horizontal flow in an aquifer, it may be possible to obtain a good model while not accounting for vertical variations of microscale and macroscale properties. Thus averaging from the microscale might be employed that is macroscopic in the lateral directions (i.e., using a length scale ℓ^{ma} such that $\ell_{\mathrm{r}}^{\mathrm{r}} \ll \ell^{\mathrm{ma}} \ll \ell^{\mathrm{me}}$), whereas the vertical averaging would be over the full vertical megascopic length scale of the system. Such a description can also be obtained by three-dimensional averaging to the macroscale followed by integration over the vertical.

For purposes of this work, attention is restricted to systems that are deterministic in that for microscale modeling all entity boundaries are completely described. At the macroscale all important properties of the system are considered to be deterministic and insensitive to small changes in the length scale, ℓ^{ma}. This representation is consistent with the classical definition of a so-called representative elementary volume (REV) [6, 10, 53, 85, 114, 120]. The actual physical size of ℓ^{ma}, and even the existence of an REV according to the requirements posed above, depends upon the characteristics of the physical system of concern.

In porous medium systems, more so than with single-phase systems, length scales relate to the physical properties of the system and the way the system is conceptualized. Selection of a microscopic length scale for modeling can result in the system being a heterogeneous construct in which flow occurs in the spaces within the solid matrix. A microscale point in the system is either in the solid or in the flow channels. Interactions between phases are accounted for through boundary conditions. Use of a macroscopic length scale for modeling, on the other hand, models the system as composed of overlapping homogeneous continua. Properties of all phases are defined at each macroscopic point, but the volumetric densities of each phase may be different at that point. The boundaries between phases in this instance have to be accounted for in some average, macroscale sense.

Based on the size of a system being considered, the data available to support a model, and the question that is being investigated, it is important to select the length scale or scales at which a problem is to be described and observed. The selection of these scales is not unique—an array of valid approaches may exist for a given system. Mathematical tools can be employed to develop models corresponding to the chosen scales. Some of these tools are described qualitatively in Subsection 1.3.5 and quantitatively in subsequent chapters.

1.2.2 Time Scales

A wide range of temporal scales occur in porous medium systems, just as is the case for spatial scales. The temporal scales of concern are suggested by the phenomena to be modeled and, sometimes, by the spatial scales of interest. For example, time scales can be related to reaction rates, the time needed to achieve equilibrium, or the volume of a fluid in a system relative to a volumetric flow rate. Chemical and biological reactions, advection, diffusion, dispersion, mass exchange, and many other processes can be bases for identification of characteristic time scales of a system. A system may have multiple time scales depending on the processes that are occurring. Elucidation of these time scales and their comparison are valuable activities that can provide considerable insight about a problem, process, or system of interest. We will consider two different types of time scales denoted, respectively, as a thermodynamic equilibrium time scale and a general time scale.

A thermodynamic time scale, designated as $\mathcal{T}_\mathrm{t}$, is a measure of the time needed for a thermodynamic property of a dynamic system to approach an equilibrium configuration. Note that boundary conditions on a system may preclude a system reaching a full thermomechanical equilibrium in which all fluxes are zero, but the thermodynamic time scale is related to the approach of thermodynamic variables to their steady state values when boundary conditions are time invariant. For example, the times required for a chemical reaction to approach equilibrium or for a thermal gradient to approach a time invariant state are thermodynamic time scales. These scales are associated with a length scale as well as some thermodynamic property of interest. Therefore a functional expression may be proposed for a property $\mathcal{P}_i$ of the form $\mathcal{T}_{\mathrm{t}i} = \mathcal{T}_{\mathrm{t}i}(\ell_i;\mathcal{P}_i)$ where ℓ_i is the length scale associated with the process and $\mathcal{T}_{\mathrm{t}i}$ is the is the thermodynamic time scale for property i. The wording “approach” equilibrium rather than “reach” equilibrium is employed in the description of the thermodynamic time scale because many mathematical descriptions of these phenomena predict that equilibrium is achieved only after an infinite amount of time. Difficulties in defining when an equilibrium state is actually reached motivates the definition of the thermodynamic time scale for a process as, essentially, a measure of the time to reach equilibrium for practical purposes. This definition, as with the selection of all scales, lacks precision yet provides an opportunity for insight to assist in selection of a useful measure of τ_{t}.[4]

A general time scale will be denoted as τ_{g} and is related to a change in some general property of the system, though not the approach of a process to equilibrium. For example, a tidal period that impacts flow in an aquifer has a general time scale, seasonal changes operate on a general time scale, releases of contamination into a site may occur at some regular intervals. Based on this short list, it can be seen that a system may have more than one general time scale. Thus, we can denote the *i*th general time scale as $\tau_{\mathrm{g}} = \tau_{\mathrm{g}}(\ell; \mathcal{P}_i)$ where $\mathcal{P}_i$ is a process or set of processes that impact time scale $\tau_{\mathrm{g}i}$ (for example, the tidal forces exerted by the sun and the moon on the earth) and ℓ_i is the length scale of observation of $\mathcal{P}_i$.

Identification of relevant time scales for several processes that might be simultaneously occurring in a system can be a challenge. However, this is an important prelude to the even more challenging task of modeling processes simultaneously occurring at disparate time scales.

Many important and useful time scales exist in porous medium systems. As an example, rates of recharge to the subsurface may be modeled on a decadal basis if one is interested in long-term groundwater depletion. Annual models are of interest if the infiltration is related to recent depletion trends. Monthly values of infiltration are important for estimates of natural irrigation impacting crop growth. Daily or hourly values of infiltration in response to a storm event are modeled when one considers watershed response. In laboratory studies or in consideration of the initiation of infiltration into a dry soil, a time scale on the order of minutes or seconds may be appropriate. Studies of unsaturated flow often involve column studies in which small changes in pressure are imposed on the system sequentially, with the system relaxing to equilibrium between each step [e.g., 23]. In such cases, the dynamics within a step occur at a smaller interval than the time required for equilibrium to be achieved. Creating links among the models formulated at different time and space scales is an active area of research.

In contrast to the spatial domain of a porous medium, the time domain is continuous without heterogeneities regardless of the scale of study. The only boundaries in the time domain are the beginning and end of the process. In some cases, one or both boundaries can be considered to be at infinity for all practical purposes. Averaging over an interval of time as well as over space does not alter the form of the equations in comparison to averaging only over space. However, one must be aware that the meanings of variables that have been time averaged are different from their

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[4] The term “thermodynamic time scale,” from a purist’s perspective, is a bit of an oxymoron. Classical thermodynamics is not concerned with times of transition between equilibrium states, kinetics, or the path taken to achieve equilibrium. It is only concerned with the fact of the existence of different equilibrium states that result from the imposition of some stress on the system and the changes in thermodynamic variables that accompany those completed transitions. Thus difficulties in defining a thermodynamic time scale do not arise in classical thermodynamics; nor does the question of how close to equilibrium a system must be to be declared to be “at” equilibrium.

meanings without time averaging. For example, a velocity with a high temporal frequency of variability will have a lower frequency after being temporally averaged. Because temporal averaging does not alter the equation forms, time averaging is not explicitly applied in the formulations employed subsequently; but one must be aware of the meanings of the various terms as averages over space and time when applying the resulting formulas.

1.3 Thermodynamically Constrained Averaging Theory Approach

In this section, we provide an overview of the TCAT approach and its elements to serve as motivation for the calculations to appear in subsequent chapters that provide the details of implementation of the method.

1.3.1 Overview

Figure 1.3 provides a schematic description of the elements of TCAT and the flow of the derivation that makes use of these elements and ties them together. This figure is color coded to indicate five different types of elements in boxes and an oval. In most cases, arrows emanating from two elements combine to produce a third element. Only production of evolution equations and of closure relations are produced directly from a single existing element. A goal of this chapter is to provide a concise qualitative roadmap of the essence of the elements in the figure and of the route to production of the TCAT model. It is essential that this description be understood. This elemental description will be referred to often and provides a preview of the need to engage in some complicated manipulations. A reader who becomes disoriented on the trip through TCAT provided by the various chapters of the book should refer to Fig. 1.3 to place the manipulations in context. Each of the elements involved with the TCAT approach is discussed in the following subsections along with an indication of how this element relates to other elements needed in the theory.

1.3.2 Microscale Conservation Principles

The methods of continuum mechanics can be used to write conservation equations for conserved quantities such as mass, momentum, angular momentum, and energy within a domain of interest [14, 32, 50, 55, 67, 71, 83, 97, 104, 109]. These approaches can also be used to write a balance equation for entropy. The entropy equation is referred to here as a “balance” equation rather than a “conservation” equation because entropy can be produced by physical processes such that a net in-

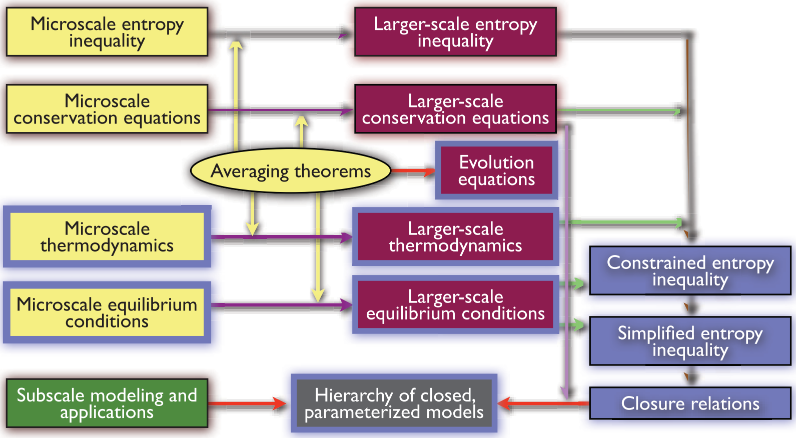

Fig. 1.3 Conceptual representation of the TCAT approach (after [46])

crease in total entropy can be achieved. The production must be accounted for in consideration of system behavior recognizing that the global amount of entropy in a closed system cannot decrease. Thus entropy is not conserved in the same sense that mass, momentum, and energy are. Continuum mechanics is used routinely to describe the behavior of phases, which occupy volumes, in terms of microscale variables. For example, such approaches are at the heart of fields such as fluid mechanics, solid mechanics, and transport phenomena. Application of dynamic continuum conservation equations for the properties of interfaces between phases and common curves are not employed extensively, although restricted forms, known as jump conditions, are commonly used to describe system behavior at discontinuities in phases [19, 29].

Conservation equations involve relating the accumulation of a conserved quantity to processes such as advective transport, non-advective transport, body sources of the quantity, boundary sources of the quantity, and production. Conservation equations can be written for a conserved property of all elements of an entity or for a species or component of the entity when a compositional system is considered. The precise forms of these conservation equations depend upon the conserved quantity of interest, the scale of the variables in the equation, the domain of the equation, and the scale at which the equation is posed. For example, formulation of a differential equation for a phase in terms of microscale quantities presumes that the locations within the domain being studied are completely occupied by that phase, whether it is a fluid or a solid phase. Appropriate conditions at the boundary of the domain must also be specified, along with needed initial conditions.

A set of continuum equations written in terms of microscale variables typically includes more unknowns than equations. Thus the equation set cannot be solved without supplementary conditions on some of the variables in the equations so that the overall number of equations and unknowns is equal. These additional equations are commonly referred to as closure relations or constitutive equations. Closure relations are independent of the conservation equations and typically provide relations among variables and derivatives of variables that appear in the equations. An example of a closure relation is an equation of state that provides an expression for fluid density as a function of pressure, temperature, and composition. Another example of a closure relation is an explicit functional form of the microscale stress tensor as a function of pressure and the rate of strain tensor. Typically, closure relations are approximate in nature and provide a description of a process that depends upon the material being considered and the dynamic conditions. The functional form employed commonly requires that values of some parameters or coefficients appearing in that form be specified. For example, the functional form of the stress tensor includes a coefficient known as the viscosity. The values, and in some cases the functional forms of these coefficients, often depend on the fluid or solid that is being modeled; and they are often referred to as material coefficients. The introduction of material dependent coefficients into approximate closure relations sets these relations apart from general conservation equations, which are exact in nature for systems written at the appropriate scales and do not contain any material parameters. Closure relations may originate from experimental, theoretical, or computational sources, or some combination of these approaches. A successful microscale continuum model is comprised of a solvable set of conservation equations, boundary conditions, and initial conditions supplemented by an approximate set of closure relations that adequately account for material properties and behavior.

After a microscale model consisting of a closed set of conservation equations has been posed, it is necessary to solve the system of resulting partial differential algebraic equations to apply the model. Analytical or numerical methods can be used to affect such solutions. These methods are outside the scope of material to be covered in this work. One very important point is that if one is concerned with describing a system at a scale larger than the microscale, there is no need to make use of microscale closure relations. Equations obtained at a larger scale will have need for closure relations, but the forms of these relations and the material coefficients that apply are generally different from microscale forms.

1.3.3 Microscale Thermodynamics

Modern thermodynamics originated as an observationally based science intended to provide a description of the behavior of engines. At its core is the fact that it describes the equilibrium state of systems at or above a continuum scale. At the microscale, this means describing, for example, the dependence of the internal energy of material in a microscale volume on the entropy, volume size, and mass. All these are extensive thermodynamic quantities that are additive. Thus, if two identical systems are combined, the values of all four of the quantities in the combined system will be double their values in each of the uncombined elements. The partial derivatives of internal energy with respect to each of entropy, volume, and mass, while holding the other two variables constant, defines the intensive thermodynamic quantities temperature, pressure, and chemical potential, respectively. If two identical systems are combined, the values of these intensive variables remain unchanged.

Starting from these elementary concepts, classical thermodynamics provides functional forms among the variables in the system. Manipulations based upon the mathematical properties of the functional forms can be used to deduce expected changes in the thermodynamic state of a system subjected to various stresses such as addition of heat, extraction of work, or a change in one of the variables. These predicted changes can be compared to observations and values of parameters that characterize a particular material, such as heat capacity or compressibility, that can be deduced. Considerable effort over the last two centuries has resulted in classical equilibrium thermodynamics becoming a well-developed and understood branch of science [7, 17, 30].

A limitation of traditional thermodynamics is the fact that it deals with systems at equilibrium; many systems of interest are not at equilibrium. The extension of thermodynamics to treat some non-equilibrium systems is known as classical irreversible thermodynamics (CIT). CIT hypothesizes that large systems that are not in formal equilibrium can be subdivided into subsystems for which the functional dependences of classical equilibrium thermodynamics apply. In other words, although the thermodynamic state of a system may be changing, the rate of change is slow enough at a local point that equilibrium relations can be used with negligible error. This hypothesis is known as the local equilibrium assumption. Its utility can be found in innumerable situations such as being able to measure the increasing temperature of a heated pot of water or stating the atmospheric pressure associated with a moving storm front. Although pressure and temperature are defined formally in the context of equilibrium systems, their near-equilibrium counterparts are found also to be very useful. Extension of thermodynamics to systems where changes are occurring rapidly or when additional variables beyond those used classically impact the thermodynamic state of the system is a continuing area of investigation. Extensions to classical thermodynamics that take into account dependence of the state of a system on previous states (memory), on fluxes, and on internal variables are among the most commonly encountered [54, 60, 69, 76, 108]. For porous medium systems we have studied, CIT, the simplest extension to classical thermodynamics, has been found to be adequate for describing the dynamics.

Differentiation of an equilibrium thermodynamic equation can be used to determine the relations among changes in variables that are consistent with the underlying equilibrium behavior of the system, globally or locally depending upon the theory and the system under consideration.

1.3.4 Microscale Equilibrium Conditions

Because microscale thermodynamics provides information about the state of a system at equilibrium, it is important to know what those conditions of equilibrium actually are. Variational methods can be used to deduce precise statements of these conditions [12, 13]. Based on this kind of analysis, one can obtain conditions of equilibrium, such as the uniformity of temperature and uniformity of the sum of the chemical plus body force potentials of a chemical species.[5] Conditions at interfaces between phases and at common curves where discontinuities exist may also be derived.

Precise statements of equilibrium conditions are useful in model formulation, especially in guiding the development of closure relations. Recall that closure relations are approximate relations among variables that appear in conservation equations needed to provide a solvable set of equations. In formulating the closure relations, it is essential to ensure that, at the very least, any approximation is consistent with equilibrium conditions. Having knowledge of what those equilibrium conditions actually are is thus very important. Armed with this information, one can consider how a variable might be modeled near equilibrium. As an example, we know that at equilibrium the non-advective heat flux in a system is zero. We also can show that at equilibrium, the temperature gradient is zero. Manipulations with the entropy balance and conservation equations, to be discussed in detail in subsequent chapters, show that the most important factor that drives a non-advective heat flux is the temperature gradient. Since we know that the temperature gradient is zero at equilibrium from a variational analysis, it is reasonable to propose as a first estimate that the non-advective heat flux is proportional to the temperature gradient. The utility of this closure approximation for a system of interest is subject to verification, but we know that the relation is valid “very close” to equilibrium. Thus experimental or computational efforts to confirm this relation are reduced to determining the definition of “very close” for a system as opposed to conditions for which a more complex closure relation might be needed. As it turns out, for many systems the linear proportionality relation is useful over a wide range of magnitudes of the temperature gradient.

Knowledge of the equilibrium conditions is used in conjunction with the entropy balance equation to suggest closure relations for many continuum systems [e.g., 24, 28]. Closure relations obtained in this framework are valid near equilibrium and do not violate the principle that dissipative processes produce entropy. Closure relations with these two properties are said to be thermodynamically consistent. The thermodynamically consistent modeling (TCM) approach incorporates closure relations of this type, and is based on a range of thermodynamic postulates. TCM contexts ranging from turbulence to solid mechanics are well-documented [e.g., 32, 50, 55, 56, 106].

The TCM approach relies upon access to conservation equations, the entropy balance, a thermodynamic formalism, and knowledge of the equilibrium state. These components of the theory are most easily assembled at the microscale. For modeling at scales above the microscale, the components of a TCM approach must be appropriate for that scale. Thus, a further requirement to ensure that the formalism to be

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[5] In this text, the primary body force potential of interest is the gravitational potential. However, the derivations are not restricted to this case and also allow for the body force to be different for each chemical species.

applied is consistent is that the microscale relations must be systematically transformed to the larger scale and incorporated into the theory such that consistency across scales is assured. TCAT is a framework that accomplishes the transition of all four elements of a TCM approach to a larger scale. In the immediately following sections, we will examine the components of TCAT that accomplish this transition.

1.3.5 Averaging Theorems

An important objective of TCAT is the consistent upscaling of microscale quantities and equations to larger spatial scales. The larger scales of concern can be macroscale, megascale, or some combination of of these two scales in different coordinate directions. For example, a fully macroscale model would be macroscale in all three spatial dimensions. A model that is megascale in the vertical direction and macroscale in the horizontal directions can be obtained by appropriate averaging. Combinations of macroscopic and megascopic averaging in each spatial direction are possible. In fact, the upscaling from the microscale need not be implemented in a particular direction such that a resultant equation set would contain microscale variability in some spatial direction; however, for porous media analyses, upscaling in all directions is employed.

In addition to selecting the length scales for modeling in each dimension, one must also consider the nature of an entity being upscaled. Entity types include fluid and solid phases that are three-dimensional at the microscale as well as interfaces, common curves, and common points, that are respectively two-, one-, and zero-dimensional at the microscale. Because upscaled forms include averaged measures, any microscale quantity can be upscaled to a combination of macroscale and megascale dimensions.

Previous work has led to a set of theorems that can be used to upscale quantities and equations for phases to the macroscale [2, 35, 52, 75, 81, 101, 113]. This set of theorems was extended to include theorems for averaging surface equations [34] to the macroscale. Subsequent work [42, 44, 79] has added to this set by providing theorems that can be employed for systematic upscaling of common curve and common point equations to the macroscale and for upscaling to the megascale and to megascale and macroscale mixes. These theorems are important in that they facilitate the conversion of averages of differential quantities to differentials of average quantities plus additional terms that account for exchanges at boundaries of entities. Application of the theorems to microscale conservation, thermodynamic, and entropy balance equations leads to larger scale equations expressed in terms of larger scale quantities that are averages over regions in some subset of space that is common to all the entities.

Complications arise when products of variables at the microscale must be upscaled because the average of a microscale product is not necessarily equal to the product of averages of each factor. However, approaches for dealing with these products have been developed in some instances. In some cases, products of variables at a larger scale can be expressed as a product of the average individual variables with a specified weighting of the average. When one factor is small relative to the other or when a factor is essentially constant, the error in expressing the average of the product as the product of averages is small. In other instances, the difference between the upscaled product of terms and the product of individually upscaled terms can be accounted for in approximate closure relations. In any event, the existence of these terms and the method chosen to account for their effects is important information that can be used when searching for possible instances where approximations have led to a model found to have shortcomings in simulating a system.

The essential notion is that averaging theorems have been developed that systematically change the scales of equations, and the variables in those equations, from the microscale to combinations of the macroscale and megascale. These theorems relate derivatives of averages to averages of derivatives and can be applied to conservation equations, the entropy balance equation, and to microscale thermodynamic expressions describing the processes occurring in phases, interfaces, or common curves. As will be discussed in Subsection 1.3.8, these theorems can also be used purely as mathematical expressions that provide relations among larger scale entity measures, such as volume fractions, interfacial area densities, and common curve length densities. These additional equations are needed if one is to have a closed system of larger scale equations that accounts for the dynamic effects due to changes in the subscale morphology and topography in a porous medium.

1.3.6 Larger-scale Conservation Principles

Microscale conservation and balance equations are transformed to a larger scale by making use of averaging theorems. The designation of an equation as "larger" scale refers to it being a representation of system behavior at a macroscale, megascale, or some combination of these two scales, all of which are larger than the microscale. Conservation of mass, momentum, angular momentum, and energy equations for phases, interfaces, common curves and common points can be written directly at the microscale. By using averaging theorems to convert equations to a larger scale, one ensures that processes and properties are all properly accounted for including geometric densities, exchanges between entities, and deviations between microscale quantities and macroscale counterparts.

When considering the microscale, a point will lie in a single entity and have properties only of that entity associated with it. At the larger scales, properties associated with a point are averages of the microscale properties of all the entities in the system in the vicinity of that point. The concept of the REV is used to determine the size of the region associated with each point. To be more precise, we can extend the usual REV concept by appending a number to indicate the number of spatial dimensions that are treated at the macroscale, while 3 minus that number will be the number of dimensions treated at the megascale. Thus REV-3 is an averaging region that is macroscopic in all three spatial dimensions; REV-2 is a larger scale averaging region that is macroscopic in two spatial dimensions and megascopic in the remaining spatial dimension; REV-1 is a larger scale averaging region that is macroscopic in one spatial dimension and megascopic in the remaining two spatial dimensions; and REV-0 is a larger scale averaging region that is megascopic in all three spatial dimensions. After averaging a microscale equation to a larger scale, all variables that appear in the equation are descriptive of the system at the larger scale. In some instances, a larger scale variable is simply the average of a microscale quantity; in other cases, the larger scale variable is an average of a microscale precursor plus some additional terms that account for microscale processes not directly observable at the larger scale.

A substantial advantage of formally averaging the microscale equations up to a larger scale rather than postulating them directly at the larger scale, as with the theory of mixtures [4, 5, 15, 47], is that the larger scale variables are expressed precisely in terms of microscale precursors. This is in contrast to the mixture theory approach wherein conservation equations are posed directly at a larger scale thus precluding the ability to connect variables across scales. Although physical intuition may lead an individual to pose a sensible multiphase model directly at the macroscale or megascale, this is most certainly not universally true. Averaging eliminates the need to invoke intuition in formulation of conservation equations at the larger scale. Additionally, in general it is not possible to infer the values and distributions of smaller scale variables from their values at a larger scale. However, with averaging, larger scale variables are known in terms of averages of smaller scale functional forms. The fact that connections among variables between scales is provided means that smaller scale measurements can be incorporated into the larger scale verification and parameterization of closed models.

The take away message is that careful averaging from the microscale to the larger scale leads to precise definitions of all variables. This quality is highly desirable in a mechanistic model that is to be used in conjunction with a physical problem of interest rather than just as a mathematical proposition.

1.3.7 Larger-scale Thermodynamics

Within the parlance of scale as employed herein, thermodynamic theories typically are developed and applied at the microscale for which a point lies entirely within a phase, in an interface, or on a common curve [84]. Since thermodynamics strictly provides information only at equilibrium about the relations among variables and about the state of the system, extensions are needed both to describe systems at larger scales and to describe them away from equilibrium. Formal averaging from the microscale to a larger scale making use of averaging theorems provides the route to obtaining macroscale thermodynamic relations that are consistent across scales. This formal procedure that provides thermodynamic relations valid at the same scale as the conservation equations is a key feature of TCAT that distinguishes it from other methods used to formulate mechanistic models at larger scales. The thermodynamic relations obtained also help in identification of macroscale conditions that must pertain if the thermodynamic relations are to be valid when the system is evolving with time or where spatial gradients in properties exist.

Although bypassing the details and mathematical challenges of rigorously changing the scale of the thermodynamic formalism is tempting, the consequences of implementing such an approach are troublesome. Nevertheless, there seem to be two primary approaches to avoiding the averaging that ensures thermodynamic consistency across scales: ignoring thermodynamics altogether and ignoring microscale thermodynamics in favor of a thermodynamic structure hypothesized directly at the larger scale.

Ignoring thermodynamics in a mechanistic modeling process may seem possible for an isothermal system. In such a case, internal energy and temperature are not modeled. Thus, if one can find a way to determine closure relations without appealing to the second law of thermodynamics, the importance of thermodynamics is eliminated. This approach has been employed in deriving equations for porous media systems involving flow, mass transport, and chemical reaction [e.g., 10, 43, 102, 115] and has also been employed in some heat transfer analyses [e.g., 86, 116]. The peril with this approach lies in the fact that information from thermodynamics is not available to guide formulation of closure relations among variables. Furthermore, the constraint provided by the second law could be violated. In any event, it would seem to be prudent to try to incorporate as much relevant information as possible into a model; and the thermodynamic behavior of fluids and solids is certainly relevant.

The other approach that is sometimes taken is an ad hoc extension of thermodynamics to the larger scale. This approach entails essentially guessing a thermodynamic form at the larger scale, usually based at least in part on the microscale form of the theory relied upon. Although this form can have the mathematical appearance of the microscale thermodynamic approach with judicious choice of notation, in fact this approach can be deficient in ascribing a physical property to each symbol [68, 69, 76, 111, 117, 118]. The lack of a transition from microscale thermodynamic expressions to macroscale forms through formal averaging is problematic because variables are not precisely defined, interscale relations of variables are not established, and the appropriate form of the equation cannot be assured. To avoid these shortcomings, TCAT requires that microscale thermodynamics be used as the foundation for establishing larger scale thermodynamics derived to be at the same scale as the larger scale conservation equations being used.

As shown in Fig. 1.3, the averaging theorems are applied to both the microscale thermodynamic equations and the microscale equilibrium conditions in order to derive the larger scale counterparts of these modeling components. The larger scale equilibrium conditions are important to know because they provide insight that is extremely helpful in postulating forms of closure relations directly at the larger scale.

1.3.8 Evolution Equations

At the larger scale certain geometric quantities emerge in model formulation, such as the volume fraction of a phase, the specific interfacial area, the specific common curve length, and the common point density. These quantities arise through the formal averaging process, are a part of larger scale mechanistic models, and are functions of time and space. In larger scale models, they replace the specification of the microscale juxtaposition of entities and their variability in time and space. They are simpler measures of phase morphology than what is observable at the microscale, and they are not as precise. These geometric quantities are additional unknowns in the conservation and thermodynamic equations in comparison to the microscale situation. Their evolution is not accounted for by conservation equations, since they are not conserved quantities. Rather the kinematics of these mathematical entities is described in terms of averages of differential geometric relations that describe microscale interface and common curve deformations. The relations are complex except for the simplest geometries [78]. For example, interfacial areas can be created and destroyed within a two-fluid porous medium system through rearrangement of the fluid phases present. Because of the complex geometry of the pore space, a description of the evolution of the growth or reduction of the interface between the fluids is not simple. In cases when the solid is fixed, the total amount of solid-fluid surface area may be constant, but the fractions of that solid surface in contact with each of the fluids can vary with time and space. Because the movement and change of geometric quantities is independent of conservation principles, the need to describe their evolution is part of the closure problem for larger scale models.

As indicated in Fig. 1.3, the purely mathematical relations provided by the averaging theorems can be used directly to produce exact equations that relate the behavior of geometric variables in various ways. These kinematic equations are referred to here as evolution equations, because they describe the changes in the geometric variables over time. Because these mathematical equations are independent of conservation and thermodynamic principles, they are of utility in addressing the larger scale closure problem. While the evolution equations derived are exact in form, they contain terms that are difficult to evaluate exactly except in very simple cases that are not achieved in porous medium problems. Therefore, approximations must be made. When the approximations are well founded and the errors in the equations are small, the evolution equations provide not only important additional constraints for producing a closed model but also physical insight into the behavior of a given system that is not available with conservation equations alone.

1.3.9 Constrained Entropy Inequality

TCAT-based model formulation makes use of an entropy inequality (EI) at the larger scale of interest. The balance of entropy for each species in each entity comprising the system can be formally averaged to the larger scale. Then, since the change of scale provides a set of balances that all apply at the same point, these equations can be added together to provide a single, larger scale entropy balance equation. Because the entropy production at a point is non-negative, the terms in the EI can be summed to be equal to the production term with the conclusion that this sum must be non-negative in accord with the second law of thermodynamics. The purpose of this arrangement of terms is to connect the mechanistic description of the dissipative processes producing entropy, such as stress, chemical species diffusion, and heat conduction, to the corresponding terms in the EI. The dissipative processes are responsible for entropy production and the terms accounting for these processes, commonly referred to as "forces," must be represented by closure relations. These terms include the stress tensor, the mass diffusive flux, and the non-advective heat flux for all the entities in the system. To make use of the EI to guide formulation of the closure relations, it is necessary to relate the entropy fluxes and generation terms that appear in the EI to fluxes and generation terms that appear in the conservation equations. Thus, the larger scale conservation equations, consisting of a collection of terms on one side of the equation that sum to zero on the other side of the equation, serve as constraints on the larger scale entropy inequality. These constraints are imposed through the use of Lagrange multipliers multiplied by the equations that are then summed with the EI. Note that since these additional equations are all identically zero, the expanded EI still holds exactly.

Although the manipulations described bring the entropy-producing terms in the conservation equations into the EI, entropy itself does not explicitly appear in any of the terms of the conservation equations. An additional relation is needed between the rate of change of entropy per volume and the rate of change of energy per volume, both of which appear in the expanded EI. Thermodynamics provides this connection. Relations among thermodynamic variables and their rates of change at the larger scale can be derived by integration of the microscale forms using averaging theorems. Then with the terms in the larger scale equation arranged such that the equation is a group of terms that sum to zero, a Lagrange multiplier can be used to impose the thermodynamic condition as an additional constraint on the EI. This summation of the entropy balance with the conservation and thermodynamic equations will be referred to as the augmented entropy inequality (AEI).

The presence of the Lagrange multipliers in the AEI provides an opportunity to cancel some terms by judicious specification of these multipliers. The goal of the specification process is to eliminate terms such that only those specifically contributing to entropy generation (i.e., irreversible processes) appear in the final form. In the TCAT approach, this means that the material derivatives in the equations are eliminated as far as possible because this isolates the surviving entropy-producing terms. The next step is solution for the forms of the Lagrange multipliers that are substituted back into the AEI to facilitate cancellation of corresponding terms. Guided by the larger scale equilibrium conditions, the equation is rearranged as possible to a sum of terms involving a product of factors that are called a thermodynamic "flux" and "force". The resulting inequality is referred to as a constrained entropy inequality (CEI).[6]

The CEI is an important expression that applies under (i) restrictions associated with the nature of phenomena being modeled (e.g., specification of the number of phases, single species, two-fluid-phase, etc.), (ii) assurance that conditions needed for the continuum approach to hold apply, and (iii) selection of the thermodynamic theory. A CEI that satisfies these three conditions is an exact expression. Although the CEI is conceptually straightforward to develop, it requires significant mathematical manipulation. Because it is exact, it provides a convenient starting point, or perhaps a restarting point, for deriving approximate closure relations after imposing a selected set of restrictions on system behavior. The existence of a CEI for a class of problems enables the development of hierarchies of models of varying sophistication without the need to reformulate the CEI from the beginning for each iteration.

1.3.10 Simplified Entropy Inequality

While the exactness property of the CEI is appealing, the equation is not strictly in the force-flux form needed for deriving closure relations. Furthermore, in some instances, subsets of the phenomena included in a CEI are not of interest, allowing for simplification of the CEI. An example would be an isothermal system such that temperature differences between entities and temperature gradients within entities are both zero. Imposition of these restrictions in describing a system simplifies the associated CEI but diminishes its generality. These kinds of restrictions are called secondary restrictions because they provide conditions on the phenomena being modeled beyond the three listed in the last section, called primary restrictions, that define the general composition of the system, its entities, and the scale of modeling.

To convert the CEI to a form consisting only of flux-force terms at the larger scale, certain terms, usually involving averages of products of microscale quantities, must be approximated. The specification of the approximation must necessarily blend physical insight and mathematical analysis if the approximation is to have utility. After secondary restrictions and subsequent approximations are applied, the equation that results is referred to as a simplified entropy inequality (SEI) which is comprised only of larger scale force-flux products for which each factor is zero at equilibrium. This is the form needed to motivate closure relations.

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[6] The quantities referred to as fluxes and forces may be scalar, vector, or tensor terms. They share the characteristic that they go to zero at equilibrium. It has been pointed out [61] that at the microscale the definitions of fluxes and forces can be permuted without impact. The main objective is to obtain a sum of products involving factors that are all zero at equilibrium. We have found that identifying various macroscale groupings as forces vs. fluxes can make the equation closure process more straightforward.

Because each form of an SEI is built on some approximations, it is more apt to change than the CEI, which is exact for a given class of problems under a set of mild conditions. A range of forms of an SEI can be obtained from a single CEI depending on the approximations imposed. For example a restriction of a general CEI to a two-species, isothermal system leads to an SEI different from that obtained considering a larger number of species in a non-isothermal system. The approximations used to derive an SEI may also change as insight develops and new approximations are proposed. The key point is that a particular exact CEI is a useful starting point for the derivation of many different SEI's that describe subsets of the general system.

1.3.11 Closure Relations

Closed mechanistic models require that the number of equations be equal to the number of unknowns in the formulation. Conservation and thermodynamic equations alone do not yield such a formulation but must be supplemented with additional equations that are called closure relations. In essence, closure relations, also referred to as constitutive equations, provide functional relations among variables existing in the equations. In relation to what has been discussed previously, variables identified as larger scale "fluxes" are expressed as functions of larger scale "forces," both of which appear in the equations. Because porous medium systems consist of phase, interface, common curve, and common point entities, the fluxes in each of these entities need to be expressed in terms of system forces. Fluxes for which closure relations are typically sought include the non-advective heat and mass transport and stress tensors. When working on macroscale or megascale porous medium systems, some fluxes are encountered that do not appear in single-phase microscale formulations. These include the relaxation rates of interface configurations to their equilibrium configurations and the stress on the solid phase surface exerted by multiple fluid phases. Parameters that arise in the process of closure relation development are commonly referred to as material coefficients. We emphasize that when closing microscale systems, microscale material coefficients such as viscosity and thermal conductivity are encountered. These coefficients are useful for modeling a system at the scale of development. However, when a system is modeled at a larger scale, the coefficients that arise account for effective processes as they impact the larger scale system behavior. Thus microscale and larger scale material coefficients are different in magnitude and in the scope of the processes being accounted for.

Because closure relations are approximations, they are not unique but rather depend on the assumptions made about system behavior. What is desired is that the closure relations be sufficiently accurate that they provide a useful description of a process of interest over a range of conditions in the system and, better yet, over a range of system types. All closure relations are required to be consistent with the second law of thermodynamics. The SEI plays a central role in assuring that proposed closure relations meet this requirement. The SEI can be examined term by term with approximations for independent fluxes being postulated that do not violate the inequality. Put another way, closure relations should never be formulated such that an independent process could destroy entropy because the second law dictates that such a situation is physically unrealistic. Closure relations may be stipulated for each independent flux to bring the number of equations up to a value closer to the number of unknowns that appear in a model. Besides the closure relations derived for dissipative processes using the SEI, additional relations are needed, such as equations of state and evolution equations, so that the total number of unknowns is matched by the total number of equations.

The material coefficients mentioned previously add a layer of complication because they are quantities that do not originally appear in the equation set. Therefore, relations are needed also for these coefficients. Typically, these coefficients are given a numerical value or a functional form in which the parameters of the form are specified. If these parameters are to be useful, they must be independently measurable or specified. In other words, if one wishes to abuse a relation between variables by assuring that it is satisfied for all cases by adjusting the parameters in the relation for the sole purpose of assuring the equality, this can be done. However, such an approach has no value in modeling a system for which all parameters should be specified based on some system characteristics. A closure relation that has parameters that are highly sensitive to system conditions, and thus a narrow range of applicability, is not useful for modeling processes as it does not describe physics. When such a situation arises one should go back to the CEI, examine the quality of the subsequent approximations made to obtain the SEI, and take steps to develop an improved closure relation.

1.3.12 Closed Models

Closed models are solvable mechanistic representations of physical systems. The models are composed of some set of conservation equations, thermodynamic relations, evolution equations, and closure relations. For such a closed model to be utilized for simulation, it must be supplemented with appropriate boundary and initial conditions so that the equations can be solved, either analytically or approximately using numerical methods. For most problems involving porous media flow, heterogeneities, coefficient variability, and the geometry of the domain being studied preclude success in obtaining analytical solutions. The literature is rich with numerical simulations of porous medium problems. These are not considered in this work. Our objective is to provide methods for development of equations that describe porous medium processes so that the numerical methods employed can be applied to appropriate equations.

Because a closed model makes use of approximations to obtain the closure conditions, caution must be exercised to ensure that the assumptions leading to the approximations apply to a specific problem of interest. Assumptions that are inappropriate for a particular situation will still lead to a set of closed, solvable equations. The simulations performed with these equations may provide appealing results. The fact that the equations being solved are the equations that “everyone uses” may add credibility. However, if the assumptions inherent in a model are not correct for a situation, the solution of the equations will not describe processes occurring in the system. The model will be inaccurate. This situation is the case with all mechanistic models regardless of how they are formulated. When ad hoc approaches are used for one or more components of the model formulation approach, the only recourse that exists when a model fails to represent adequately a system of concern is to try different ad hoc approaches.

The TCAT framework, in contrast to ad hoc and other procedures, provides the opportunity to systematically revise models because all elements are developed by upscaling and all restrictions and approximations are specifically noted. If a simulation based on TCAT equations is found to be inadequate, all assumptions made in formulating the model can be reexamined because they are explicit. Experimental and computational work can be undertaken to support or refute assumptions employed in producing an SEI from a CEI. The need for a higher order closure relation for a particular flux may be identified with the resultant form motivated by the SEI. Porous medium systems of concern are complicated and multiscale in nature. Therefore the need to iterate on the formulation of a model should be expected and, indeed, be a tool that helps identify the parts of a system that are not well understood. The TCAT framework ensures that a path for completely systematic and scientific analysis of models can be found.

1.3.13 Subscale Modeling and Applications

Model validation is a process whereby a mechanistic model is compared to a system that it is intended to represent. In many environmental systems, the validation process can include the comparison of a model with a system, or set of systems, that is experimentally observed for the purpose of sequentially isolating important elements of the system. By performing comparisons between the model and experimental results, over a range of conditions, the breadth of conditions for which a model form is valid can be established. The broader the range for which a model is valid, the more confidence one can have in the model, and the greater its utility.

For an increasing number of multiscale systems, computational validation is possible. In many cases it is possible to simulate a porous medium system at the microscale where all phase distributions are known and evolve with time. One widely used method for microscale simulation is the lattice Boltzmann method [e.g., 1, 21, 48, 49, 57, 62–66, 70, 74, 87, 89, 90, 99, 100, 103, 105, 107, 112, 119, 121]. Another makes use of pore network models that attempt to capture the key morphological features of a porous medium system of interest [e.g., 8, 72, 88, 93, 95, 98]. When the physics are well-described at the microscale and the computational tools used to approximate the microscale situation are sufficiently accurate, the behavior of a system can be simulated with high fidelity. The microscale simulations provide a basis for determining larger scale parameters and variables. They also provide guidance in postulating specific forms of larger scale closure relations that may only be known in a general functional form. Thus subscale modeling and simulation plays an important role both in constructing final forms of TCAT models and in validating conditions under which the models are of utility.

If a larger scale TCAT model fails to describe a system well enough to answer questions about the system behavior, microscale simulation can assist in determining the cause of the failure. The dense information available from a microscale simulation can be useful in pinpointing the restriction or approximation imposed on the TCAT model that must be revisited. Modeling multiphase flow in porous media is difficult. Bringing to bear a variety of consistent methods to address the problem provides synergistic potential for identifying and gaining understanding of processes and hence advancing the state of modeling.

1.4 Summary

In this chapter, we have introduced an overview of the basic qualitative notions essential for understanding the TCAT approach to formulating mechanistic models at scales larger than the microscale. Each component of TCAT involves significant mathematical manipulations. By outlining these components and their individual role in the model formulation process, the foundation has been laid for a complete conceptual understanding of the TCAT approach to be developed and applied in this book. Our hope is that this conceptual understanding will provide a safe haven if the reader finds that the mathematical details of the theory seem to lose context.

We intend that this book will facilitate understanding and implementation of TCAT at a variety of levels. If the conceptual bases of TCAT are properly understood, it will not be necessary for a reader of this book to understand all of the details of every component of TCAT in order to use or even develop useful TCAT models. For example, the body of TCAT work accomplished to date has resulted in the derivation of several CEI's and SEI's, along with a large number of conservation equations, at larger scales. If one understands the TCAT process at a qualitative level, these available results can be used as a starting point for model formulation and verification. Similarly, a reader may wish to focus on the verification of a given TCAT model by performing microscale simulations. The available formulation, restrictions, and approximations provide a means to accomplish such a validation with rigor.

The ambitious reader will choose to master all aspects of TCAT. This class of reader will need to thoroughly understand the overview presented in this chapter and also the details of each of the components of the theory. Introductions to these details are included in the chapters that follow, while additional details can be gained by reference to the growing TCAT literature [36–41, 45, 58, 59, 79, 80]. This book is not a self-contained encyclopedia of TCAT details, including very lengthy and, at times, tedious calculations. Rather, it is a gateway to the method that will hopefully make engagement with many compelling and subtle aspects of the approach more feasible.

Exercises

1.1. How many data points would be needed to image the solid phase skeleton at a resolution of 6 microns, the same resolution employed in producing Fig. 1.1, for a three-dimensional region that is 1 m on a side?

1.2. Provide an example of a property that exhibits length scale dependence. Prepare a sketch of the value of that property as a function of length scale and explain the behavior.

1.3. For each of the following systems

- identify the physical description of each of the five length scales introduced in Eq. (1.1);
- identify a question that could be addressed appropriately by developing a model at each scale; and
- identify a question that could be addressed appropriately by a developing a model that makes use of more than one scale.

a. fuel cell
b. water supply aquifer
c. river
d. watershed
e. petroleum reservoir

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Chapter 2
Microscale Conservation Principles

2.1 Overview

TCAT models are developed by formally upscaling conservation and balance equations, thermodynamic relations, and equilibrium conditions from the microscale to a macroscale, a megascale, or some combination of the two scales. A prerequisite of a TCAT implementation is thus the full set of microscale equations that are to be upscaled. The purpose of this chapter is to provide the necessary understanding and forms of the microscale conservation and balance equations. Microscale thermodynamics will be presented in Chap. 3 and the microscale equilibrium conditions will be developed in Chap. 4.

Recall that the microscale is sufficiently large to allow the use of a continuum, rather than a molecular, representation of the physical system and sufficiently well resolved that the geometry of each entity is completely represented. This means that phases are viewed as being juxtaposed and a geometric description of the regions occupied by each phase is employed. The interfacial areas between phases, common curves where three phases come together, and common points where four phases come together are all parts of the problem description. Solution for the locations of the boundaries of the phases may be necessary for the microscale problem (i.e., for the case of a moving boundary problem [4]). Certain extensive quantities are known to be conserved or balanced within each of the entity types. Extensive properties of a system, such as mass, momentum, angular momentum, energy, entropy, and electrical charge, are additive.[1] The total amount of an extensive quantity in a system is the sum of the amounts of the extensive quantity associated with each element of the system. Intensive quantities are not additive. For example, temperatures, pressures, and chemical potentials are not additive. A system that is formed as a combination of two identical systems possesses twice the amount of extensive properties of each contributing system, while the intensive properties of the individual and combined

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[1] Although conservation of electrical charge is an important principle that has applicability in porous media problems such as fuel cells and capillary electrochromatography [5, 11, 13], this is not covered in this book.

W. G. Gray and C. T. Miller, *Introduction to the Thermodynamically Constrained Averaging Theory for Porous Medium Systems,* Advances in Geophysical and Environmental Mechanics and Mathematics, DOI: 10.1007/978-3-319-04010-3_2,

systems are the same. Conservation and balance equations are not derived for intensive quantities, only for extensive quantities. Conservation and balance equations describe the rate of change of the amount of an extensive quantity in a region. They account for flows of the property into and out of the region as well as sources and generation of the quantity. Formulation of these equations in terms of microscale properties is the subject of this chapter.

Traditional treatments of conservation principles are primarily concerned with conservation of properties of a phase. Exchanges between phases at interfaces between phases are accounted for by jump conditions [e.g., 6]. Our study adopts a more comprehensive approach. For porous medium problems, the dynamics of processes occurring at microscale discontinuities, including interfaces, common curves, and common points, are important to the system behavior. By their nature, porous media are highly heterogeneous from a microscale perspective due to these discontinuities. Thus, it is imperative that all important features of conservation and balance principles involving these entities be accounted for in larger scale equations, as well as at the microscale. Therefore, we will make use of general conservation and balance equations not only for phases but also for interfaces, common curves, and common points. Conservation principles will be developed for material in an entity as a whole and also based on each species that may be present in an entity. Summation of the species-based forms of conservation relations will provide the entity-based forms; for an entity consisting of a single chemical species, the entity- and species-based forms are identical.

The ability to account for processes occurring in regions of discontinuity between phases in porous media is conceptually appealing. However, in practice this ability comes only with significant overhead due to the expansion in the number of conservation equations that must be employed. A brief count will reinforce this notion. There are four different types of entities: phases, interfaces, common curves, and common points. For each entity, we can consider three types of conservation and balance equations by formulating them for each chemical species, for an entity composed of a single chemical species, and by considering the entity equations as accounting for the behavior of all species collectively. This suggests that 12 different classes of equations exist. For each of these 12 classes there are nine conservation or balance equations, excluding conservation of charge. These are the scalar mass conservation, energy conservation, and entropy balance equations plus the vector momentum and angular momentum equations, each of which consists of three components. Thus, we can potentially form 108 different conservation or balance equations. For common points, the radius of possible rotation is zero so that we need not consider the nine possible equation types of angular momentum counted above. Thus, there are 99 equations that may potentially be employed in modeling a system. All of these equations are not needed to describe a given system (e.g., for a single-fluid-phase porous media system, no common curves or common points exist; if one employs conservation equations for all species in an entity, the entity-based equation is not needed). For some systems, more than 99 equations will be employed since species-based equations can be employed for each chemical species present in each entity. By considering the differences in the full set of equations, however, we will have a basis for selection of equations to be used to model a system of interest. The focus of this chapter is on providing examples of the derivation of the equations and on listing the equations of importance.

Several approaches exist for deriving the microscale conservation and balance equations. One approach is to derive a general conservation equation for each type of entity and to specify the appropriate mapping between the general conservation equation and the physical phenomena of interest for a particular conservation equation. We will follow this approach because it provides the opportunity to minimize the calculations that must be performed in comparison to ignoring similarities and developing equations for each conserved quantity by independent calculations.

2.2 General Conservation and Balance Principles

This section proceeds by first presenting a conceptual conservation or balance equation that describe the physical processes that must be considered in the formulation of an appropriate equation. Then, in the subsequent subsections, the conceptual physical description provided is translated into a mathematical form that is appropriate for each of the four types of entities.

2.2.1 General Qualitative Formulation

Because we are interested in changes with time of extensive properties, we will develop equations that describe the rate of change of a property in a domain of interest. A change in the amount of a property in a region must be due to advective transport of the property across the boundary, the rate at which the property is added within the domain due to body sources, non-advective boundary fluxes of the property, and generation of the property within the domain. These mechanisms can be combined in a conceptual balance equation that accounts for the rate of change of the extensive property within a domain as

$$\begin{aligned}&\begin{bmatrix}\text{Rate of}\\ \text{Accumulation}\end{bmatrix}+\begin{bmatrix}\text{Net Outward}\\ \text{Advective Flux}\end{bmatrix}-\begin{bmatrix}\text{Body}\\ \text{Sources}\end{bmatrix}\\ &\quad-\begin{bmatrix}\text{Non-advective}\\ \text{Boundary Sources}\end{bmatrix}-\begin{bmatrix}\text{Rate of}\\ \text{Generation}\end{bmatrix}=0\,. \end{aligned}\tag{2.1}$$

The dimensions, or units, of Eq. (2.1) are the dimensions of the extensive property being considered per time. The challenge is to convert this verbal equation into an appropriate and useful mathematical form. The ease with which this can be done depends on the extensive property that is being conserved and physical insight about the forms of the source and generation terms. Insight exists based on the shared human experience over centuries that has resulted in detailed studies of physical systems including highly resolved experimental results and computational analyses across many scales.

Equation (2.1) can be used to formulate microscale conservation equations by first considering a megascale region whose boundary is resolved at the microscale. There are several aspects of this region that should be noted. The extent and location of the region are not necessarily fixed. Note, however, that for the extensive property of interest to enter (or exit) the region, it must be transported in a direction normal to the boundary of the region. Thus, the normal velocity of advective transport at the boundary relative to the velocity of the boundary is important, not just the velocity alone. Advection tangent to the surface, or normal to the surface but at the same velocity as the normal velocity of the boundary, will not result in a flux of a property of interest into or out of the system. The boundaries of a region need not be coincident with any physical boundary, but can be located as is convenient or desirable to identify a particular study region. For example, a portion of an interface between phases may be considered rather than the entire interface; or a volume can be considered that moves through a larger system at some selected velocity to model the rate of change of the extensive property in that volume. For convenience here, though not generally required, the domains will be selected such that microscale properties are continuous within the region and are first-order differentiable with respect to space. If a fluid is in a porous medium, the microscale domain chosen is such that it consists exclusively of that fluid. An interface between fluids, for example, will be studied in a surficial domain that contains only that interface type. Additionally, the requirement of first order differentiability is employed so that the normal to an interface domain is unique and the tangent to a common curve is unique. This condition does not preclude the ability to consider piecewise continuous or disconnected regions in identifying a domain. For the continuum mechanical approach taken here, small changes in the size of a region should in turn lead to small changes in respective extensive quantities.

2.2.2 General Quantitative Formulation

Suppose it is desired to develop a conservation equation for an extensive property in a region Ω with boundary Γ. When considering a phase, Ω is a volumetric region with surface Γ; for an interface property, Ω is a surface region with bounding curve Γ; for a curve, Ω is a one-dimensional region with end points at Γ. Note that while a volume always has a boundary, a closed surface or a closed common curve will not have a boundary. Common points have no boundaries. Now designate the extensive property of interest as $\mathbb{F}$. Furthermore, let the point value per unit region (i.e., the density of $\mathbb{F}$) be indicated as F. Thus for a spatial domain, F has units of the extensive property per unit volume; while for a surficial domain, F has units of the extensive property per unit area; and so forth. In formulating a balance equation, it is important to take into account the fact that although $\mathbb{F}$ is an extensive quantity, it may vary at the microscale throughout the region such that $\mathbb{F}$ is not necessarily equal to the product of F at any given point in Ω and the extent of the integration region, which could be a volume, area, length, or number of points depending upon the type of entity represented by Ω. Additionally, the material within the region might not have a uniform microscale velocity; and the fluxes at the boundary are not necessarily uniform across the boundary. Thus, the successful development of a conservation equation with units of the extensive quantity per unit time must depend upon integral expressions over the domains and their boundaries. For example, the extensive property, $\mathbb{F}$, is related to its density distribution within a domain, F, according to

$$\mathbb{F} = \int\limits_{\Omega} F \, \mathrm{d}\mathfrak{r} \,. \tag{2.2}$$

The rate of accumulation term in Eq. (2.1) for extensive property $\mathbb{F}$ is expressed as

$$\begin{bmatrix} \text{Rate of} \\ \text{Accumulation} \end{bmatrix} = \frac{\mathrm{d}\mathbb{F}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Omega} F \, \mathrm{d}\mathfrak{r} \,. \tag{2.3}$$

The net rate of advective transport out of Ω is related to the advective flux across the boundary, Γ. Denote the advective velocity as $\mathbf{v}$, the velocity of the boundary of the domain as $\mathbf{w}$ and the unit normal vector to the boundary oriented to be positive outward as $\mathbf{n}$. The amount of $\mathbb{F}$ that will cross the boundary depends upon the density distribution F at the boundary and the normal advective velocity, $\mathbf{v}\cdot\mathbf{n}$, relative to the normal velocity of the boundary, $\mathbf{w}\cdot\mathbf{n}$. The rate of depletion of $\mathbb{F}$ in the region of interest due to advective flux across the boundary, the second term in Eq. (2.1), is

$$\begin{bmatrix} \text{Net Outward} \\ \text{Advective Flux} \end{bmatrix} = \int\limits_{\Gamma} F \left(\mathbf{v} - \mathbf{w} \right) \cdot \mathbf{n} \, \mathrm{d}\mathfrak{r} \,. \tag{2.4}$$

It is helpful to realize that the sign of $\left(\mathbf{v} - \mathbf{w} \right) \cdot \mathbf{n}$ determines whether the flux is into (negative) or out of (positive) the region.

The body source rate of supply of $\mathbb{F}$ per unit of domain is denoted $S_{\Omega T}$, where the subscript T indicates that we are considering the total body source which can be broken into components as will be seen subsequently. The rate of generation within the body per unit of domain is denoted G_{Ω}. These two quantities may be integrated over the domain so that the third and fifth terms in Eq. (2.1) are expressed as

$$\begin{bmatrix} \text{Body} \\ \text{Sources} \end{bmatrix} + \begin{bmatrix} \text{Rate of} \\ \text{Generation} \end{bmatrix} = \int\limits_{\Omega} S_{\Omega T} \, \mathrm{d}\mathfrak{r} + \int\limits_{\Omega} G_{\Omega} \, \mathrm{d}\mathfrak{r} \,. \tag{2.5}$$

The supply of $\mathbb{F}$ at the boundary due to processes other than advection still involves transfer across the boundary and therefore is in the direction normal to the boundary. Because non-advective transport may also occur in directions tangent to the boundary, it is important to isolate the component of this transport that is normal to the boundary. The non-advective transfer of $\mathbb{F}$ per unit of boundary in the normal direction is denoted as $\mathbf{S}_\Gamma \cdot \mathbf{n}$ so that the fourth term in Eq. (2.1) is accounted for as

$$\begin{bmatrix} \text{Non-advective} \\ \text{Boundary Sources} \end{bmatrix} = \int\limits_{\Gamma} \mathbf{S}_\Gamma \cdot \mathbf{n} \, \mathrm{d}\mathfrak{r} \, . \tag{2.6}$$

Substitution of Eqs. (2.3)–(2.6) into Eq. (2.1) yields the general conservation equation,

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Omega} F \, \mathrm{d}\mathfrak{r} + \int\limits_{\Gamma} F \, (\mathbf{v} - \mathbf{w}) \cdot \mathbf{n} \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega} S_{\Omega T} \, \mathrm{d}\mathfrak{r} - \int\limits_{\Gamma} \mathbf{S}_\Gamma \cdot \mathbf{n} \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega} G_\Omega \, \mathrm{d}\mathfrak{r} = 0 \, . \tag{2.7}$$

The particular forms that the integrands take in this equation depend upon the extensive quantity being conserved or balanced and the geometric dimensionality of the region being considered.

Equation (2.7) provides a good beginning point to develop conservation and balance equations for properties of entities as a whole, whether those entities be volumes, surfaces, curves, or common points. A small twist has to be accommodated in considering common curves and points due to their geometric character. For instance, the boundary of a curve is the points at the end of the curve. Thus the integral over the boundary of a common curve has to be simplified to be explicitly represented as a sum over the end points of the curve. This issue will be treated in detail when developing the equations for the common curve explicitly.

2.2.3 Species-based Quantitative Formulation

In most porous medium systems of interest, a phase will consist of multiple species. For example, a water phase may contain not only hydrogen and oxygen, but also a wide range of other inorganic and organic species—hundreds of different species in some cases. Species-based models are important under two conditions. First, the composition of a phase may be of interest intrinsically. This would be the case if a species in the phase were a contaminant of interest and it were important to model the spatial and temporal distribution of the species. Second, the composition of a phase can influence its physical or chemical properties and hence its behavior. For example, changes in the mass fraction of an inorganic salt can affect the density or viscosity of a water phase. Similar comments apply for other entities as well. Therefore, species-based, or compositional, porous medium models can be important.

In the interest of generality, we will be developing conservation and balance equations for the properties of individual species in an entity. The species-based equations can be obtained by identification of the chemical species processes corresponding to terms in Eq. (2.7). The equations obtained apply directly for the single-species and multiple-species situations. Summation of a species conservation equation over all species impacting the entity yields a conservation or balance equation for the entity as a whole. Here we provide the general species-based form. The "derivation" involves little more than the introduction of some subscript notation into Eq. (2.7).

Because we are studying species in phase, interface, common curve, and common point entities, it is helpful to make use of notation that identifies both the species and the entity of interest. We will make use of subscripts to designate quantities of interest as being microscale properties.[2] The subscript i is used to designate an individual chemical species from among the full set of chemical species in the system. The subscript α is used to indicate the entity that is being considered. For example, in the general equation, $F_{i\alpha}$ would be the density of the microscale property of interest for chemical species i in entity α. The domain of all species in entity α is Ω_α and the boundary of that domain is Γ_α. Neither the domain nor the boundary depends on the chemical species being considered in the entity. The outwardly directed normal from the boundary of Ω_α is the unit vector $\mathbf{n}_\alpha$. Each chemical species may have a different advective velocity so that the velocity of species i in entity α is designated as $\mathbf{v}_{i\alpha}$. Although each species may have a different velocity, thereby requiring the use of subscript i to differentiate among the species present, the velocity of the boundary of the domain is species independent. Therefore, the boundary velocity is denoted as $\mathbf{w}_\alpha$. The body source, non-advective surface source, and the generation terms in Eq. (2.7) all may depend on the species being considered and the entity. Therefore, the subscript $i\alpha$ will be appended to each of these. Thus, the general conservation equation for an extensive property of a chemical species in an entity α can be written in terms of microscale variables as:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega_\alpha} F_{i\alpha}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_\alpha} F_{i\alpha}\left(\mathbf{v}_{i\alpha}-\mathbf{w}_\alpha\right)\cdot\mathbf{n}_\alpha\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha} S_{\Omega T i\alpha}\,\mathrm{d}\mathfrak{r} \\ - \int\limits_{\Gamma_\alpha} \mathbf{S}_{\Gamma i\alpha}\cdot\mathbf{n}_\alpha\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha} G_{\Omega i\alpha}\,\mathrm{d}\mathfrak{r} = 0 \quad \text{for } i\in\mathfrak{I}_s, \alpha\in\mathfrak{I}\,, \qquad (2.8)\end{aligned}$$

where $\mathfrak{I}_s$ is the set of species indices and $\mathfrak{I}$ is the set of entity indices, which includes the indices of phases ($\mathfrak{I}_\mathrm{P}$), interfaces ($\mathfrak{I}_\mathrm{I}$), common curves ($\mathfrak{I}_\mathrm{C}$), and common points ($\mathfrak{I}_\mathrm{Pt}$) such that $\mathfrak{I} = \mathfrak{I}_\mathrm{P}\cup\mathfrak{I}_\mathrm{I}\cup\mathfrak{I}_\mathrm{C}\cup\mathfrak{I}_\mathrm{Pt}$. We will refer to all of the sets of indices as index sets.

With Eq. (2.8) as a starting point, we will make use of theorems that allow equations for an entire entity to be localized so that they apply at any point in the entity. The theorems depend on the dimensionality of the entity. The entity types will be considered in turn, starting with phases and proceeding in order to entities of lower dimensionality. We will then identify the quantities that appear in the general equations based on the processes of interest so that they are particularized to the members of the set of conservation and balance equations.

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[2] It is perhaps premature, but may be helpful, to note that while subscripts are used for microscale quantities, superscripts will be used to designate larger scale quantities in subsequent chapters.

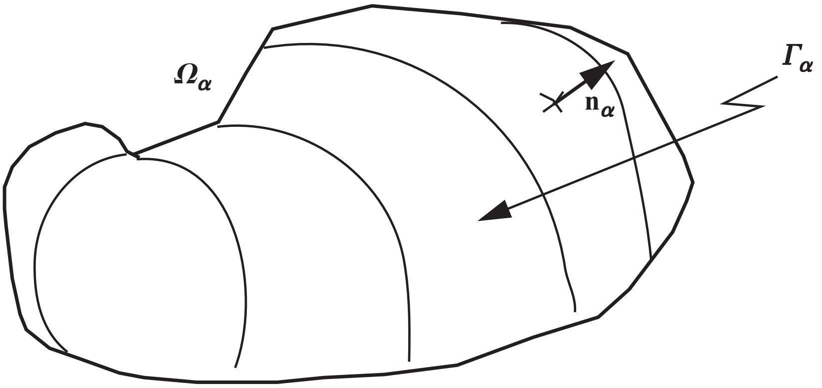

Fig. 2.1 Arbitrary closed volume $\Omega_\alpha \subset \mathrm{I\!R}^3$ containing phase $\alpha \in \mathfrak{I}_\mathrm{P}$ with boundary $\Gamma_\alpha \subset \mathrm{I\!R}^2$. Unit vector $\mathbf{n}_\alpha$ is normal to Γ_α and oriented to be positive outward from Ω_α

2.3 Conservation and Balance Principles for a Phase

The objectives of this section, which focuses on conservation and balance equations for phases, are twofold. First, the general conservation equation for a species-based extensive property given in Eq. (2.8) will be changed from the given form appropriate for a phase as a whole to a form that is appropriate at any microscale point in the phase. Second, particular forms of the conservation and balance equations will be developed for mass, momentum, energy, and entropy.

2.3.1 General Microscale Point Forms

The study of conservation of a property of an α phase, where $\alpha \in \mathfrak{I}_\mathrm{P}$, requires that the region of study, Ω_α with boundary Γ_α be a closed volume, as depicted in Fig. 2.1. The fact that this phase occupies volume can be expressed as $\Omega_\alpha \subset \mathrm{I\!R}^3$, which states that the domain is in three-dimensional real space. The extent of α is the volume it occupies, $\mathbb{V}_\alpha$. The boundary is a two-dimensional surface, implying that $\Gamma_\alpha \subset \mathrm{I\!R}^2$, and the extent of Γ_α is measured by the area $\mathbb{A}_{\alpha\alpha}$. The double subscript on $\mathbb{A}$ is used to indicate the total boundary area of Ω_α, regardless of any other phase or phases also contacting Γ_α.

Equation (2.8) can be focused further for the specific case of species-based conservation of a phase property and then reduced to a point form. With just the minor tweak of restricting $\mathfrak{I}$ to be $\mathfrak{I}_\mathrm{P}$, and with proper identification of the integrand terms, Eq. (2.8) becomes a statement of mass, momentum, or energy conservation, or an entropy balance, for a species in a phase. Each of these equations will be formulated after first reducing the equation to point form.

The conversion of Eq. (2.8), with $\mathcal{J}$ restricted to $\mathcal{J}_P$, to the form that applies at a point within a phase requires that the surface integral terms be converted to volume integrals. This task can be accomplished making use of mathematical theorems. Because a variety of theorems will be relied upon in this work, we adopt a previously established convention to name these theorems [8, 12] of the form $<letter>[i,(j,k),l]$. For a transport theorem $<letter>$ is T while $<letter>$ is replaced by D for a divergence theorem. Gradient theorems, which are similar to divergence theorems, replace $<letter>$ with G. Theorems involving material derivatives and averages of deviations between quantities at different scales are designated as M theorems. The index i indicates the dimensionality of the microscale domain, j refers to the number of macroscale dimensions that make use of differential operators, k is the number of macroscale dimensions over which integration occurs, and l is the number of megascale dimensions. For the theorems of this chapter, conversion is from the megascale, with integrals over the entire domain, to integrals over the microscale. Thus both j and k are zero.

Two theorems are employed to eliminate the surface integrals in Eq. (2.8). The transport theorem is as follows [3, 8, 10, 15]:

Theorem 2.1 (T[3,(0,0),3]) *For a smooth continuous and differentiable function f defined over a domain $\Omega_\alpha \subset \mathbb{R}^3$ that may deform with time t due to velocity $\mathbf{w}_\alpha$ of closed boundary Γ_α with outward normal from the boundary $\mathbf{n}_\alpha$,*

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega_\alpha(t)} f\,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_\alpha(t)} \frac{\partial f}{\partial t}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_\alpha(t)} f\mathbf{w}_\alpha\cdot\mathbf{n}_\alpha\,\mathrm{d}\mathfrak{r}\,. \tag{2.9}$$

Physically, when f is the density of some conserved quantity, the left side of Eq. (2.9) represent the change in the total amount of the conserved quantity with time over the entire domain. This change is accounted for on the right side by changes of the property density within Ω_α and movement of the domain boundary Γ_α that could affect both the location of Ω_α where changes in f are being studied and the size of $\mathbb{V}_\alpha$.

Also of use for manipulations with integrals over the boundary of the domain is the divergence theorem [3, 8, 10, 15]:

Theorem 2.2 (D[3,(0,0),3]) *For a smooth continuous and differentiable tensor function $\mathbf{f}$ defined over a domain $\Omega_\alpha \subset \mathbb{R}^3$ that may deform with time t due to velocity $\mathbf{w}_\alpha$ of closed boundary Γ_α with outward normal from the boundary $\mathbf{n}_\alpha$,*

$$\int\limits_{\Omega_\alpha(t)} \mathrm{div}\,\mathbf{f}\,\mathrm{d}\mathfrak{r} = \int\limits_{\Gamma_\alpha(\mathrm{t})} \mathbf{f}\cdot\mathbf{n}_\alpha\,\mathrm{d}\mathfrak{r}\,, \tag{2.10}$$

where div *is a divergence operator that contracts the last index of* $\mathbf{f}$.

If $\mathbf{f}$ is a vector or a symmetric second order tensor, then $\mathrm{div}\,\mathbf{f}$ may be written equivalently as $\nabla\cdot\mathbf{f}$. In general, if $\mathbf{f}$ is a second order tensor, $\mathrm{div}\,\mathbf{f}$ is equal to $\nabla\cdot\mathbf{f}^{\mathrm{T}}$, where the superscript $^{\mathrm{T}}$ indicates the transpose. Physically, Eq. (2.10) equates the sum of the net outward fluxes from all points within the spatial domain on the left side to the flux across the domain boundary on the right side.

With f replaced by $F_{i\alpha}$, and $\mathbf{f}$ replaced by $F_{i\alpha}\mathbf{v}_{i\alpha}$ in one instance and by $\mathbf{S}_{\Gamma i\alpha}$ in another, Eqs. (2.9) and (2.10) can be used to eliminate the surface integrals from Eq. (2.8) giving

$$\int\limits_{\Omega_\alpha} \left[\frac{\partial F_{i\alpha}}{\partial t} + \nabla\cdot(\mathbf{v}_{i\alpha}F_{i\alpha}) - S_{\Omega T i\alpha} - \operatorname{div}\mathbf{S}_{\Gamma i\alpha} - G_{\Omega i\alpha} \right] \mathrm{d}\mathfrak{r} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{P} \,. \tag{2.11}$$

For a phase, the body source does not include fluxes from adjacent entities that act as body sources because a point within a phase is not in contact with any other entities; other entities are encountered only at the boundary of the phase. The portion of the total body source that is independent of adjacent entities is designated as $S_{\Omega i\alpha}$, such that, for a phase,

$$S_{\Omega T i\alpha} = S_{\Omega i\alpha} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{P} \,. \tag{2.12}$$

Because the integration volume is arbitrary, Eq. (2.11) must hold for any volume that is sufficiently large to meet the previously noted continuum hypothesis requirements. This fact implies that the integrand itself must be zero at each microscale point within the volume. Recall that a value of a microscale quantity at a point implies an average about a volume with a length scale that is long compared to the mean distance between molecules. Thus the general point conservation equation for an extensive property of a species per unit microscale volume in a phase is

$$\frac{\partial F_{i\alpha}}{\partial t} + \nabla\cdot(\mathbf{v}_{i\alpha}F_{i\alpha}) - S_{\Omega i\alpha} - \operatorname{div}\mathbf{S}_{\Gamma i\alpha} - \mathrm{G}_{\Omega i\alpha} = 0, \quad \text{for } i \in \mathfrak{I}_\mathrm{s}, \alpha \in \mathfrak{I}_\mathrm{P} \,. \tag{2.13}$$

This equation may also be written equivalently using the material derivative as

$$\frac{\mathrm{D}_{i\alpha}F_{i\alpha}}{\mathrm{D}t} + F_{i\alpha}\mathbf{I}{:}\mathbf{d}_{i\alpha} - S_{\Omega i\alpha} - \operatorname{div}\mathbf{S}_{\Gamma i\alpha} - \mathrm{G}_{\Omega i\alpha} = 0, \quad \text{for } i \in \mathfrak{I}_\mathrm{s}, \alpha \in \mathfrak{I}_\mathrm{P} \,, \tag{2.14}$$

where the material derivative is defined as

$$\frac{\mathrm{D}_{i\alpha}}{\mathrm{D}t} = \frac{\partial}{\partial t} + \mathbf{v}_{i\alpha}\cdot\nabla \,; \tag{2.15}$$

the symmetric rate of strain tensor for species i in phase α is defined as

$$\mathbf{d}_{i\alpha} = \frac{1}{2}\left[\nabla\mathbf{v}_{i\alpha} + (\nabla\mathbf{v}_{i\alpha})^\mathrm{T}\right] \,; \tag{2.16}$$

and $\mathbf{I}$ is the unit tensor. Because our interest in the microscale is primarily to provide equations for transformation to the larger scale, we will work mostly with microscale equations in the form of Eq. (2.13) because mathematical theorems for change in scale are more directly available for the partial time derivative than the material derivative. We emphasize, however, that Eqs. (2.13) and (2.14) are exactly equivalent.

When a phase consists of only one chemical species, the subscript i may be deleted from Eqs. (2.13)–(2.16) to obtain the general equation for a phase. When a phase is composed of multiple species, a conservation equation for a property of the phase as a whole may be obtained by summing all the conservation equations for that property based on the species present. Then judicious choice of the variables deemed to be characteristic of the phase as a whole, rather than of species-based properties, results in the phase-based conservation equation. This procedure is best accomplished based on the particular property being conserved or balanced to ensure that the phase-based variables are properly defined in terms of the species-based variables.

2.3.2 Specific Conservation and Balance Principles

Specific conservation and balance equations can be derived directly from general Eq. (2.13), or the equivalent form given by Eq. (2.14), by selecting a property to be conserved or balanced and then specifying the mapping between the general variables in the equations and specific applicable physical quantities. These quantities must be specified such that all of the operative processes that affect the conservation or balance principle are included in the equation. The discussion here will focus on the physical basis for the respective mapping assignments, and the resulting equation forms will be listed.

The mappings for conservation of species mass, momentum, and energy and for the balance of species entropy are given in Table 2.1. A notation that will prove to be convenient is introduced such that $\mathcal{M}$, $\mathcal{P}$, $\mathcal{E}$, $\mathcal{S}$, and $\mathcal{G}$ represent equations for conservation of mass, momentum, and energy, and balance of entropy and gravitational potential, respectively, written in partial time derivative form. Additionally, we make use of the notation $\mathcal{M}_*$, $\mathcal{P}_*$, $\mathcal{E}_*$, $\mathcal{S}_*$, and $\mathcal{G}_*$ to denote the corresponding, and equivalent, equations written using material derivatives. In the table each of the conservation equation types is subscripted with the species qualifier, $i \in \mathfrak{I}_s$, and the entity qualifier, $\alpha \in \mathfrak{I}_{\mathrm{P}}$ to indicate that the equations apply to that species and phase.

Conservation and balance equations for phase entities accounting for the species collectively rather than individually are given in Table 2.2. Each of the properties appropriate for the conservation equation of interest is given. Note that the sum of a set of species-based equations for a property over all species present is equal to the corresponding phase-based equation. Based on this fact, it is tempting to think that an entry in Table 2.2 is equal to the sum over all species of the corresponding entry in Table 2.1. However this is not so for all terms! Rather the relations between the phase-based and species-based terms must be determined carefully such that multiple definitions for a designated quantity do not arise.

Table 2.1 can be used along with Eq. (2.13) or Eq. (2.14), which are repeated for convenience at the top of the table, to write a full set of species-based conservation

Table 2.1 Physical variables for species-based phase equations in partial derivative or material derivative form. $\mathcal{M}_{i\alpha}$, $\mathcal{P}_{i\alpha}$, $\mathcal{E}_{i\alpha}$, $\mathcal{S}_{i\alpha}$, and $\mathcal{G}_{i\alpha}$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential for species i in phase α

$$\mathcal{F}_{i\alpha} = \frac{\partial F_{i\alpha}}{\partial t} + \nabla\cdot(\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega i\alpha} - \operatorname{div}\mathbf{S}_{\Gamma i\alpha} - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_{\mathrm{P}}$$

or

$$\mathcal{F}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha} F_{i\alpha}}{\mathrm{D}t} + F_{i\alpha}\mathbf{l}{:}\mathbf{d}_{i\alpha} - S_{\Omega i\alpha} - \operatorname{div}\mathbf{S}_{\Gamma i\alpha} - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_{\mathrm{P}}$$

$\mathcal{F}_{i\alpha}$	$F_{i\alpha}$	$S_{\Omega i\alpha}$	$\mathbf{S}_{\Gamma i\alpha}$	$G_{\Omega i\alpha}$
$\mathcal{M}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha}$	—	—	$r_{i\alpha}$
$\mathcal{P}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha}$	$\mathbf{t}_{i\alpha}$	$\mathbf{p}_{i\alpha} + r_{i\alpha} \mathbf{v}_{i\alpha}$
$\mathcal{E}_{i\alpha}$	$E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}$	$\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha} + h_{i\alpha}$	$\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\cdot\mathbf{v}_{i\alpha} + \mathbf{q}_{i\alpha}$	$e_{i\alpha} + \mathbf{p}_{i\alpha}\cdot\mathbf{v}_{i\alpha} + r_{i\alpha} \frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}$
$\mathcal{S}_{i\alpha} - \Lambda_{i\alpha}$	$\eta_{i\alpha}$	$b_{i\alpha}$	$\boldsymbol{\varphi}_{i\alpha}$	$\Lambda_{i\alpha}$
$\mathcal{G}_{i\alpha}$	$\Psi_{i\alpha}$	$-\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha}$	—	$\rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} + r_{i\alpha} \psi_{i\alpha}$

and balance equations for a phase. For example, making use of the table, one obtains the equation of conservation of mass of a chemical species in partial time derivative form as:

$$\mathcal{M}_{i\alpha} = \frac{\partial(\rho_\alpha \omega_{i\alpha})}{\partial t} + \nabla\cdot(\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}) - r_{i\alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_{\mathrm{P}} , \tag{2.17}$$

where ρ_α is the mass density equal to mass of α phase per volume of α phase; $\omega_{i\alpha}$ is the mass fraction of species i in phase α (i.e., the fraction of the mass of the phase that is due to the presence of species i); and the generation term, $r_{i\alpha}$, accounts for the set of reactions that produce species i in phase α by conversion from other species. Many simultaneous reactions that either produce or consume species i may be operative. Therefore, $r_{i\alpha}$ is a variable that represents the net result of some set of intraphase biogeochemical reactions. The precise form of these reactions will be system dependent, and the mathematical representation of $r_{i\alpha}$ may be mechanistically rigorous or an approximation that tries to account for the important elements of the reaction. One example of an approximate relation for $r_{i\alpha}$ would be the representation of a complex reaction pathway by only accounting for the rate-limiting step. Another case is the approximation of a higher order reaction by a lower order expression when the mass fraction of one of the reactants is approximately constant. Simplifications of these types are commonplace. Finally, note that in Eq. (2.17) there are no non-advective sources of the species because the only mechanisms for modification of the amount of a chemical constituent at a point are advection and reaction.

The species mass conservation equation in material derivative form, $\mathcal{M}_{*i\alpha}$, may also be obtained directly from Table 2.1 as

Table 2.2 Physical variables for entity-based phase equations in partial derivative or material form. $\mathcal{M}_\alpha$, $\boldsymbol{\mathcal{P}}_\alpha$, $\mathcal{E}_\alpha$, $\mathcal{S}_\alpha$, and $\mathcal{G}_\alpha$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential in phase α

$$\mathcal{F}_\alpha = \frac{\partial F_\alpha}{\partial t} + \nabla\cdot(\mathbf{v}_\alpha F_\alpha) - S_{\Omega\alpha} - \nabla\cdot\mathbf{S}_{\Gamma\alpha} - \sum_{i\in\mathfrak{I}_s} G_{\Omega i\alpha} = 0 \quad \text{for } \alpha\in\mathfrak{I}_\mathrm{P}$$

or

$$\mathcal{F}_{*\alpha} = \frac{\mathrm{D}_\alpha F_\alpha}{\mathrm{D}t} + F_\alpha \mathbf{l}{:}\mathbf{d}_\alpha - S_{\Omega\alpha} - \nabla\cdot\mathbf{S}_{\Gamma\alpha} - \sum_{i\in\mathfrak{I}_s} G_{\Omega i\alpha} = 0 \quad \text{for } \alpha\in\mathfrak{I}_\mathrm{P}$$

$\mathcal{F}_\alpha$	F_α	$S_{\Omega\alpha}$	$\mathbf{S}_{\Gamma\alpha}$	$G_{\Omega i\alpha}$
$\mathcal{M}_\alpha$	ρ_α	—	—	—
$\boldsymbol{\mathcal{P}}_\alpha$	$\rho_\alpha\mathbf{v}_\alpha$	$\rho_\alpha\mathbf{g}_\alpha$	$\mathbf{t}_\alpha$	—
$\mathcal{E}_\alpha$	$E_\alpha + \rho_\alpha\left(\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2} + K_{E\alpha}\right)$	$\rho_\alpha\mathbf{g}_\alpha\cdot\mathbf{v}_\alpha + h_\alpha$ $+ \sum_{i\in\mathfrak{I}_s} \rho_\alpha\omega_{i\alpha}\mathbf{u}_{i\alpha}\cdot\mathbf{g}_{i\alpha}$	$\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha + \mathbf{q}_\alpha$	—
$\mathcal{S}_\alpha - \Lambda_\alpha$	η_α	b_α	$\boldsymbol{\varphi}_\alpha$	$\Lambda_{i\alpha}$
$\mathcal{G}_\alpha$	Ψ_α	$-\rho_\alpha\mathbf{g}_\alpha\cdot\mathbf{v}_\alpha - \sum_{i\in\mathfrak{I}_s} \rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{u}_{i\alpha}$	$-\sum_{i\in\mathfrak{I}_s} \rho_\alpha\omega_{i\alpha}\psi_{i\alpha}\mathbf{u}_{i\alpha}$	$\rho_\alpha\omega_{i\alpha}\frac{\partial\psi_{i\alpha}}{\partial t}$ $+r_{i\alpha}\psi_{i\alpha}$

$$\mathcal{M}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha}(\rho_\alpha\omega_{i\alpha})}{\mathrm{D}t} + \rho_\alpha\omega_{i\alpha}\mathbf{l}{:}\mathbf{d}_{i\alpha} - r_{i\alpha} = 0 \quad \text{for } i\in\mathfrak{I}_s, \alpha\in\mathfrak{I}_\mathrm{P}\ . \tag{2.18}$$

Mathematically, this equation is equivalent to Eq. (2.17), and the two equations are interchangeable. Throughout the text, however, we will be careful to make use of the notation $\mathcal{M}_{i\alpha}$ vs. $\mathcal{M}_{*i\alpha}$ to distinguish between the forms of the species conservation equation being employed. In many cases, one form as opposed to the other is more appropriate for a particular analysis.

There are a couple of ways to obtain an equation of mass conservation for the α entity as a whole as in the $\mathcal{M}_\alpha$ row in Table 2.2. For example, the material derivative form for mass conservation is

$$\mathcal{M}_{*\alpha} = \frac{\mathrm{D}_\alpha\rho_\alpha}{\mathrm{D}t} + \rho_\alpha\mathbf{l}{:}\mathbf{d}_\alpha = 0 \quad \text{for } \alpha\in\mathfrak{I}_\mathrm{P}\ . \tag{2.19}$$

Note that there are no terms specific to any species or any chemical reaction term in this equation. Unlike the species mass, which can be generated by transformation from a different chemical species, the total mass of all species combined in an entity is not impacted by reactions such that

$$\sum_{i\in\mathfrak{I}_s} r_{i\alpha} = 0\ . \tag{2.20}$$

Although Eq. (2.19) applies whether or not a phase is composed of multiple species, it cannot distinguish among the conservation behaviors of different species. If there is only one species present, then the species-based and phase-based equations are equivalent since $\omega_{i\alpha} = 1$, $\mathbf{v}_{i\alpha} = \mathbf{v}_\alpha$, and $r_{i\alpha} = 0$ in the species-based equation.

Even though the conservation equation for a phase can be obtained as a sum over all the species, this process is not as direct using the material derivative forms as with the partial derivative forms. This is because the velocity in the material derivative can be different for each species. Thus, it is easiest to obtain the phase-based mass conservation equation from the species-based form as

$$\mathcal{M}_\alpha = \frac{\partial \rho_\alpha}{\partial t} + \nabla\cdot(\rho_\alpha \mathbf{v}_\alpha) = 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \tag{2.21}$$

by summing Eq. (2.17) over all species. By making use of the fact that, by definition, the sum of the mass fractions of all species is 1 such that

$$\sum_{i\in\mathfrak{I}_s} \omega_{i\alpha} = 1 , \tag{2.22}$$

and by choosing $\mathbf{v}_\alpha$ to be the velocity of the center of mass of the material, the barycentric velocity, defined as

$$\mathbf{v}_\alpha = \sum_{i\in\mathfrak{I}_s} \omega_{i\alpha}\mathbf{v}_{i\alpha} , \tag{2.23}$$

one obtains Eq. (2.21). Then Eq. (2.19) is obtained directly from Eq. (2.21) by making use of the definition of the material derivative. We can also define the diffusion velocity of a chemical species, $\mathbf{u}_{i\alpha}$, as the species velocity relative to the barycentric velocity such that

$$\mathbf{u}_{i\alpha} = \mathbf{v}_{i\alpha} - \mathbf{v}_\alpha . \tag{2.24}$$

Therefore Eqs. (2.23) and (2.24) can be combined to show that the diffusion velocity must satisfy the constraint that

$$\sum_{i\in\mathfrak{I}_s} \omega_{i\alpha}\mathbf{u}_{i\alpha} = \mathbf{0} . \tag{2.25}$$

These last two equations dictate that for a system composed of N chemical constituents, only $N-1$ of the mass fractions and diffusion velocities are independent; the remaining value of each can be calculated, respectively, from Eqs. (2.22) and (2.25).

Tables 2.1 and 2.2, respectively, can be used to obtain the conservation of momentum vector equation for a species in a phase

$$\begin{aligned}\mathcal{P}_{i\alpha} = \frac{\partial(\rho_\alpha\omega_{i\alpha}\mathbf{v}_{i\alpha})}{\partial t} &+ \nabla\cdot(\rho_\alpha\omega_{i\alpha}\mathbf{v}_{i\alpha}\mathbf{v}_{i\alpha}) - \rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha} - \nabla\cdot\mathbf{t}_{i\alpha}{}^{\mathrm{T}} \\ &- \mathbf{p}_{i\alpha} - r_{i\alpha}\mathbf{v}_{i\alpha} = \mathbf{0} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{P} ,\end{aligned} \tag{2.26}$$

and for the phase as a whole[3]

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[3] Because it is somewhat tangential to our objectives here, we will not prove that the stress tensor for an entity is symmetric while the species-based stress tensor is not necessarily symmetric. In the

$$\mathcal{P}_\alpha = \frac{\partial(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \nabla\cdot(\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha) - \rho_\alpha \mathbf{g}_\alpha - \nabla\cdot\mathbf{t}_\alpha = \mathbf{0} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,, \tag{2.27}$$

where $\mathbf{t}$ is the stress tensor, $\mathbf{g}$ is the body force per unit mass, and $\mathbf{p}_{i\alpha}$ represents the interspecies transfer of momentum from all other species within phase α to species i.

The conservation of momentum equation relates the change in momentum per volume to the advective transport of momentum, surface forces, body forces, and, for the species-based equation, to inter-species momentum transfer processes. The stress tensor accounts for the effects of material behavior in response to surface forces that act on the entity, such as pressure and frictional effects. The mathematical form of the stress tensor depends upon material properties and is approximated by what is called a constitutive or closure relation. The body force per unit mass accounts for the effects of gravity, Coriolis effects, and electromagnetic forces that act at all points within the entire domain of the phase, Ω_α. While the conservation equation formulated can include all of these body forces, we are primarily concerned with gravitational effects.

Just as $r_{i\alpha}$ represents the net effect of all reactions on the mass production rate of species i per volume, $\mathbf{p}_{i\alpha} + r_{i\alpha}\mathbf{v}_{i\alpha}$ includes two terms that account for the net transfer of momentum from all other species to species i due to interspecies collisions and reactions, respectively.[4] The net transfer to all species must be zero such that

$$\sum_{i\in\mathfrak{I}_s} (\mathbf{p}_{i\alpha} + r_{i\alpha}\mathbf{v}_{i\alpha}) = \mathbf{0} \,. \tag{2.28}$$

The body force per unit mass for the phase, $\mathbf{g}_\alpha$ is the barycentric sum of the forces acting on each species with

$$\mathbf{g}_\alpha = \sum_{i\in\mathfrak{I}_s} \omega_{i\alpha}\mathbf{g}_{i\alpha} \,. \tag{2.29}$$

Because momentum transferred between species does not impact the total momentum of the system, the sum of the transfer term over all species must be zero. It is a useful exercise to show that obtaining Eq. (2.27) from Eq. (2.26) by summing over all species requires that the entity-based stress tensor be related to the species-based stress tensor according to:

$$\mathbf{t}_\alpha = \sum_{i\in\mathfrak{I}_s} (\mathbf{t}_{i\alpha} - \rho_\alpha \omega_{i\alpha}\mathbf{u}_{i\alpha}\mathbf{u}_{i\alpha}) \,. \tag{2.30}$$

Tables 2.1 and 2.2 can also be used directly to state the conservation of energy equations for a species in a phase and for a phase, respectively, as

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entity-based equations, either the stress tensor or its transpose may be used equivalently because of symmetry [1, 7, 9].

[4] A different perspective on the velocity that should multiply $r_{i\alpha}$ in the generation term of Eq. (2.26) has been provided in [16]. However, this issue is not important if one notes that a complementary definition of $\mathbf{p}_{i\alpha}$ can account for any choice of velocity.

$$\begin{aligned}\mathcal{E}_{i\alpha} =& \frac{\partial}{\partial t}\left(E_{i\alpha}+\rho_\alpha\omega_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right)+\nabla\cdot\left[\left(E_{i\alpha}+\rho_\alpha\omega_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right)\mathbf{v}_{i\alpha}\right]\\ &-\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha}-h_{i\alpha}-\nabla\cdot\left(\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\cdot\mathbf{v}_{i\alpha}+\mathbf{q}_{i\alpha}\right)\\ &-e_{i\alpha}-\mathbf{p}_{i\alpha}\cdot\mathbf{v}_{i\alpha}-r_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}=0\quad\text{for } i\in\mathfrak{I}_s, \alpha\in\mathfrak{I}_{\mathrm{P}}\end{aligned}\tag{2.31}$$

and

$$\begin{aligned}\mathcal{E}_{\alpha} =& \frac{\partial}{\partial t}\left[E_\alpha+\rho_\alpha\left(\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}+K_{E\alpha}\right)\right]+\nabla\cdot\left\{\left[E_\alpha+\rho_\alpha\left(\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}+K_{E\alpha}\right)\right]\mathbf{v}_\alpha\right\}\\ &-\rho_\alpha\mathbf{g}_\alpha\cdot\mathbf{v}_\alpha-\sum_{i\in\mathfrak{I}_s}\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{u}_{i\alpha}-h_\alpha-\nabla\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha\right)=0\quad\text{for } \alpha\in\mathfrak{I}_{\mathrm{P}}\,.\end{aligned}\tag{2.32}$$

In these equations, E is the internal energy per volume, which is due to random molecular motion and the chemical bonds present; $K_{E\alpha}$ is a kinetic energy term due to velocity fluctuations of the species relative to the barycentric velocity of the phase; $\mathbf{q}$ is the non-advective heat flux; h is an energy body source term (e.g. radiation); and $e_{i\alpha}$ accounts for the internal energy transferred to species i from all other species. We note that the net transfer of internal and kinetic energy (due to collisions and reaction) among all the species present must be zero such that

$$\sum_{i\in\mathfrak{I}_s}\left(e_{i\alpha}+\mathbf{p}_{i\alpha}\cdot\mathbf{v}_{i\alpha}+r_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right)=0\,.\tag{2.33}$$

The energy equation warrants careful consideration to ensure that it is well understood on a physical basis. Consider Eq. (2.32), the microscale conservation of energy equation for a phase. The quantity being conserved is the sum of internal and kinetic energy. Internal energy of a phase is obtained as the sum of the species internal energies with

$$E_\alpha=\sum_{i\in\mathfrak{I}_s}E_{i\alpha}\,.\tag{2.34}$$

Kinetic energy for the phase equation has two components. The leading order component, $\rho_\alpha\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha/2$, is based on the barycentric velocity of the phase and the density of the phase. The second component, $\rho_\alpha K_{E\alpha}$, provides an addition to this term due to the deviations of the individual species velocities from the barycentric velocity of the phase. To gain insight into this situation, consider a microscale point where the barycentric velocity as defined in Eq. (2.23) is zero. The case that $\mathbf{v}_\alpha=0$ does not imply that all species velocities are zero but merely that the sum of these velocities weighted by their respective mass fractions is zero. Kinetic energy does not depend on the direction of the velocities as it only involves velocity squared. Thus the deviations of species velocities from the barycentric velocity make a contribution to kinetic energy beyond that of the barycentric velocity. By summing Eq. (2.31) over all species and requiring that the result provides the conservation of phase energy equation, one can show that

$$K_{E\alpha} = \sum_{i \in \mathfrak{J}_s} \omega_{i\alpha} \frac{\mathbf{u}_{i\alpha} \cdot \mathbf{u}_{i\alpha}}{2} \,. \tag{2.35}$$

The first divergence term in Eq. (2.32) accounts for the net outward flux of internal plus kinetic energy resulting from advective transport. The non-advective surface sources of energy are included in the next divergence term. The first of these terms is $\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha$, where $\mathbf{t}_\alpha$ is the same quantity defined in Eq. (2.30). This is the rate of work done on the system per volume due to surface forces resulting from stress. This interpretation follows because stress is a force per area and the product with velocity yields the rate of work per area. The second non-advective flux is $\mathbf{q}_\alpha$, and it is the heat flux into the system that contributes to a change in the system energy. The heat flux vector is another quantity for which a closure relation is needed.

The product $\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha$ is a body source of energy. The product $\rho_\alpha \mathbf{g}_\alpha$ is a force per volume and the dot product of this product with velocity yields a rate of work per volume. If the force per volume is different for each species in the system, the summation term in Eq. (2.32) will contribute an additional body source due to a non-uniform distribution of chemical species in the system. The energy of a system can also be influenced by an additional type of body source, which is indicated as h_α. This source accounts for non-mechanical physical processes such as radiative transport. The dimensions of this term are energy contributed to the system per volume per time. By using the fact that the sum of the body source terms based on the species over all species must equal the body source terms for the phase, one obtains

$$h_\alpha = \sum_{i \in \mathfrak{J}_s} h_{i\alpha} \,. \tag{2.36}$$

Terms similar to those described above for the phase-based energy equation appear also in the species-based form of Eq. (2.31). The physical descriptions of the terms are similar, although they pertain to species rather than to the entity as a whole. One important difference is the presence of the last three terms on the left side of Eq. (2.31) that account for inter-species transfer of energy. The quantity $r_{i\alpha} \mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}/2$ accounts for the rate of change in kinetic energy of the species per volume that accompanies a chemical reaction. The term $\mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$ is the rate of work done on species i due to collisions with other species. Finally, $e_{i\alpha}$ accounts for any other contributions of energy to species i due to interactions with other species. Because these terms all involve inter-species exchanges of energy, their collective sum over all species must be zero, as stated in Eq. (2.33).

Finally, with $\mathbf{t}_\alpha$ defined as in Eq. (2.30), one can show that in terms of species-based quantities,

$$\mathbf{q}_\alpha = \sum_{i \in \mathfrak{J}_s} \left\{ \mathbf{q}_{i\alpha} + \left[\mathbf{t}_{i\alpha}{}^{\mathrm{T}} - \left(E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{u}_{i\alpha} \cdot \mathbf{u}_{i\alpha}}{2} \right) \mathsf{I} \right] \cdot \mathbf{u}_{i\alpha} \right\} \,. \tag{2.37}$$

This equation states that some processes associated with species movement relative to the barycentric velocity are accounted for on a phase basis as part of the non-advective surface source. We have stated that $\mathbf{q}_\alpha$ is a “heat” flux vector, and this is the case if one considers the apparent mechanical processes in brackets to be subscale sources of energy. Alternatively, one can recognize that $\mathbf{q}_\alpha$ is composed of heat conduction effects plus energy transport due to variability in the species velocities.

The species-based and entity-based entropy balances for a phase can be obtained, respectively, from Tables 2.1 and 2.2 as

$$\mathcal{S}_{i\alpha} = \frac{\partial \eta_{i\alpha}}{\partial t} + \nabla\cdot(\eta_{i\alpha}\mathbf{v}_{i\alpha}) - b_{i\alpha} - \nabla\cdot\boldsymbol{\varphi}_{i\alpha} = \Lambda_{i\alpha} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{P} \tag{2.38}$$

and

$$\mathcal{S}_{\alpha} = \frac{\partial \eta_{\alpha}}{\partial t} + \nabla\cdot(\eta_{\alpha}\mathbf{v}_{\alpha}) - b_{\alpha} - \nabla\cdot\boldsymbol{\varphi}_{\alpha} = \Lambda_{\alpha} \geq 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \, , \tag{2.39}$$

where η is the entropy per volume, $\boldsymbol{\varphi}$ is an entropy flux vector, b an entropy source, and Λ is an entropy generation rate.

Entropy is postulated to be an extensive thermodynamic variable and thus the balance equation is written for an entropy density, which is consistent in form with the conservation equations. The balance equations account for the rate of change of entropy, the advective flux, the non-advective flux, the body source and, on the right side, a generation term. In Eq. (2.38), $\Lambda_{i\alpha}$ accounts for exchange of entropy of species i with other species in addition to the generation of entropy by irreversible, dissipative processes. Because it is impacted by both these processes, $\Lambda_{i\alpha}$ can be either positive or negative.

Summation of the species entropy equation over all species yields Eq. (2.39). The definitions of the phase-based variables in terms of the species-based quantities are:

$$\eta_\alpha = \sum_{i\in\mathfrak{I}_s} \eta_{i\alpha} \, , \tag{2.40}$$

$$\boldsymbol{\varphi}_\alpha = \sum_{i\in\mathfrak{I}_s} (\boldsymbol{\varphi}_{i\alpha} - \eta_{i\alpha}\mathbf{u}_{i\alpha}) \, , \tag{2.41}$$

$$b_\alpha = \sum_{i\in\mathfrak{I}_s} b_{i\alpha} \, , \tag{2.42}$$

and

$$\Lambda_\alpha = \sum_{i\in\mathfrak{I}_s} \Lambda_{i\alpha} \, . \tag{2.43}$$

In contrast to the situation with the conservation equations where the sum over the species of generation terms equals zero, the sum of the generation terms for the entropy balance is non-zero. The portion of $\Lambda_{i\alpha}$ that is due to entropy exchanges between species will sum to zero, but the portion that is due to irreversible processes will sum such that $\Lambda_\alpha \geq 0$. The non-negative character of the right side of Eq. (2.39) indicates that entropy is not a conserved quantity. The generation rate per volume, Λ_α, will be zero only when all processes in the system are occurring reversibly (e.g., at equilibrium). In other instances Λ_α will be non-zero and is required to be non-negative by the second law of thermodynamics.

One other equation that will prove useful is the relation between the rate of change of the body force potential energy per unit volume and the body force per unit mass. Because the body force potential, usually specified to be the gravitational potential, does not appear in any of the conservation equations, we have to develop an additional condition based on mathematical identities, conservation of mass, and the definition of the body force per volume in terms of the potential.

The body force potential per unit volume of species i in phase α, $\Psi_{i\alpha}$, is defined as

$$\Psi_{i\alpha} = \rho_\alpha \omega_{i\alpha} \psi_{i\alpha} \; . \tag{2.44}$$

Application of the product rule to this identity yields the definition of $\mathcal{T}_{\mathcal{G}*i\alpha}$ as

$$\mathcal{T}_{\mathcal{G}*i\alpha} = \frac{\mathrm{D}_{i\alpha}\Psi_{i\alpha}}{\mathrm{D}t} - \psi_{i\alpha}\frac{\mathrm{D}_{i\alpha}(\rho_\alpha\omega_{i\alpha})}{\mathrm{D}t} - \rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}_{i\alpha}\psi_{i\alpha}}{\mathrm{D}t} = 0 \; . \tag{2.45}$$

We may also define the body force potential per mass, ψ_α, and the body force potential, Ψ_α, on entity bases, respectively, as

$$\psi_\alpha = \sum_{i\in\mathfrak{I}_s} \omega_{i\alpha}\psi_{i\alpha} \tag{2.46}$$

and

$$\Psi_\alpha = \sum_{i\in\mathfrak{I}_s} \rho_\alpha\omega_{i\alpha}\psi_{i\alpha} = \sum_{i\in\mathfrak{I}_s} \Psi_{i\alpha} = \rho_\alpha\psi_\alpha \; . \tag{2.47}$$

The material derivative of Ψ_α, taken using the α phase velocity, is

$$\mathcal{T}_{\mathcal{G}*\alpha} = \frac{\mathrm{D}_\alpha\Psi_\alpha}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s} \psi_{i\alpha}\frac{\mathrm{D}_\alpha(\rho_\alpha\omega_{i\alpha})}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s} \rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}_\alpha\psi_{i\alpha}}{\mathrm{D}t} = 0 \; . \tag{2.48}$$

Another useful expression relates the change in potential to gravity and mass conservation. This will be obtained next. The species mass conservation equation in terms of a material derivative, $\mathcal{M}_{*i\alpha}$ as given in Eq. (2.18), may be used to eliminate $\mathrm{D}_{i\alpha}(\rho_\alpha\omega_{i\alpha})/\mathrm{D}t$ from Eq. (2.45). Also the definition of the material derivative in Eq. (2.15) may be used to expand $\mathrm{D}_{i\alpha}\psi_{i\alpha}/\mathrm{D}t$ so that we convert Eq. (2.45) to

$$\frac{\mathrm{D}_{i\alpha}\Psi_{i\alpha}}{\mathrm{D}t} + \psi_{i\alpha}\left(\rho_\alpha\omega_{i\alpha}\mathbf{l}{:}\mathbf{d}_{i\alpha} - r_{i\alpha}\right) - \rho_\alpha\omega_{i\alpha}\frac{\partial\psi_{i\alpha}}{\partial t} - \rho_\alpha\omega_{i\alpha}\mathbf{v}_{i\alpha}\cdot\nabla\psi_{i\alpha} = 0 \; . \tag{2.49}$$

The body force potential per unit mass of species i in phase α, $\psi_{i\alpha}$, is related to the body force per mass, $\mathbf{g}_{i\alpha}$, according to

$$\nabla\psi_{i\alpha} + \mathbf{g}_{i\alpha} = \mathbf{0} \; . \tag{2.50}$$

Substitution of this identity into Eq. (2.49) and use of the definition provided in Eq. (2.44) provides the microscale balance equation for the body force potential of chemical species i in phase α,

$$\mathcal{G}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha}\Psi_{i\alpha}}{\mathrm{D}t} + \Psi_{i\alpha}\mathbf{l}{:}\mathbf{d}_{i\alpha} + \rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha} - \rho_\alpha\omega_{i\alpha}\frac{\partial\psi_{i\alpha}}{\partial t} - r_{i\alpha}\psi_{i\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{P}} \,. \tag{2.51}$$

This equation has attributes that make it similar in form to the conservation and balance equations. Thus its elements have been collected as appropriate, and the equation appears in Table 2.1.

For the phase entity, summation of $\mathcal{G}_{i\alpha}$ over all species and rearrangement into material derivative form yields

$$\begin{aligned}\mathcal{G}_{*\alpha} =& \frac{\mathrm{D}_\alpha\Psi_\alpha}{\mathrm{D}t} + \Psi_\alpha\mathbf{l}{:}\mathbf{d}_\alpha + \nabla\cdot\left(\sum_{i\in\mathfrak{I}_s}\rho_\alpha\omega_{i\alpha}\psi_{i\alpha}\mathbf{u}_{i\alpha}\right) + \rho_\alpha\mathbf{g}_\alpha\cdot\mathbf{v}_\alpha \\ &+ \sum_{i\in\mathfrak{I}_s}\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{u}_{i\alpha} - \sum_{i\in\mathfrak{I}_s}\rho_\alpha\omega_{i\alpha}\frac{\partial\psi_{i\alpha}}{\partial t} - \sum_{i\in\mathfrak{I}_s} r_{i\alpha}\psi_{i\alpha} = 0 \\ &\text{for } \alpha \in \mathfrak{I}_{\mathrm{P}} \,. \end{aligned} \tag{2.52}$$

2.4 Conservation and Balance Principles for an Interface

Interfaces are the second type of entity of interest in the development of conservation and balance equations. Interfaces are the regions in a multiphase system that exist at the boundary between two phases. Because interfaces are boundaries of three-dimensional entities, they are two-dimensional objects. As a result of their dimensionality, interfaces do not occupy any volume in a system. This makes the notion of conservation principles within an interface seem, perhaps, a bit elusive.

Different phases contain matter in different states and typically of different chemical composition. As a result of these differences, a heterogeneity in composition and resulting chemical forces can exist at the interface between two phases. Correspondingly, physical quantities such as density, mass fractions, and others can change significantly as one moves from the interior of one phase to the interior of an adjoining phase. This transition region is treated conceptually as an interface. Quantities that are assigned to an interface account mechanistically for underlying heterogeneous molecular structure and forces. Some species, such as surfactants, accumulate at interfaces so the molecular structure may be very different at the boundary between two phases from that in the bulk phase; there is always a transition from the composition in one bulk phase to the composition in another bulk phase.

Furthermore, in multiphase systems, interfaces play a crucial role as the location where mass, momentum, energy, and entropy can be exchanged between adjoining phases. The extent of the interfacial area thus affects the degree and rate at which exchanges occur and can easily be seen to be a crucial quantity in the description of system behavior. Conventional multiphase models do not explicitly model the full dynamics of interfaces and interface properties, although jump conditions between phases are commonly formulated. By formulating conservation and balance equations for interfaces, we will produce the fundamental relations needed to properly account for the impacts of interfaces between phases.

In this section, conservation and balance laws for interfaces will be developed. As with the study of phases, general conservation equations will first be presented. Then particular forms of these equations will be tabulated and discussed for both species-based and entity-based equations of mass, momentum, and energy conservation along with the entropy and body force potential balances.

2.4.1 General Microscale Point Form

The study of conservation of an interfacial property is developed for a surface domain, Ω_α, with boundary curve Γ_α, where $\alpha \in \mathfrak{I}_\mathrm{I}$ as depicted in Fig. 2.2. This notation specifies that α is in the index set of interfaces, such that $\Omega_\alpha \subset \mathrm{I\!R}^2$. This means that the interface is a surface in two-dimensional space. The extent of Ω_α is designated as the area $\mathbb{A}_\alpha$. The boundary curve is a one-dimensional entity such that $\Gamma_\alpha \subset \mathrm{I\!R}^1$. Its extent is measured by the length $\mathbb{L}_{\alpha\alpha}$. Interfaces exist as the boundary between two phases. If the phases on each side of the interface α are designated as $\beta \in \mathfrak{I}_\mathrm{P}$ and $\gamma \in \mathfrak{I}_\mathrm{P}$ then $\Omega_\alpha = \bar{\Omega}_\beta \cap \bar{\Omega}_\gamma$ where the overbar on Ω indicates a union of a domain with its boundary, for example, $\bar{\Omega}_\beta = \Omega_\beta \cup \Gamma_\beta$. At points on the interface, outward normal vectors from each adjacent phase can be denoted as $\mathbf{n}_\beta$ and $\mathbf{n}_\gamma$ where $\mathbf{n}_\beta = -\mathbf{n}_\gamma$. On Γ_α, outwardly directed unit vectors from Ω_α that are normal to Γ_α and tangent to Ω_α are denoted as $\mathbf{n}_\alpha$. The interface moves with velocity $\mathbf{w}_\alpha$. However, $\mathbf{w}_\alpha \cdot \mathbf{n}_\beta = \mathbf{v}_\alpha \cdot \mathbf{n}_\beta$ on Ω_α because a microscale particle on the interface whose normal velocity is different from the normal velocity of the interface will no longer be on the interface and thus does not contribute to the measure of the velocity of the interface. The tangential velocity of material in the interface need not be equal to the tangential velocity of the interface. The velocity of the boundary of the interface in the direction tangent to the interface and normal to Γ_α, $\mathbf{w}_\alpha \cdot \mathbf{n}_\alpha$, relates to the stretching or contracting of the interface at its edges. Flow can occur across this boundary, in the same way that flow crosses the boundary of a volume, so that this velocity is not necessarily equal to the velocity of flow. Conservation and balance equations associated with an interface must necessarily take into account the translation and deformation of the interface.

With the preceding definitions and considerations, a species-based general conservation or balance equation follows directly from Eq. (2.8) as

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Omega_\alpha} F_{i\alpha}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_\alpha} F_{i\alpha} \left(\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha\right) \cdot \mathbf{n}_\alpha\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha} S_{\Omega T i\alpha}\,\mathrm{d}\mathfrak{r}$$

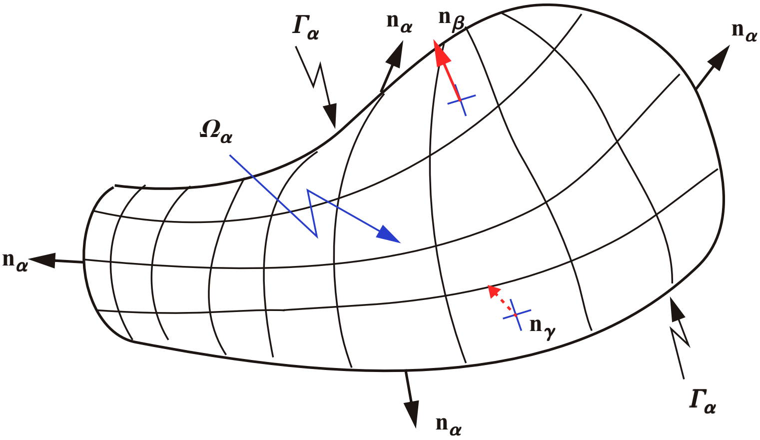

Fig. 2.2 Arbitrary finite, non-closed surface in the region $\Omega_\alpha \subset \mathbb{R}^2$ containing interface $\alpha \in \mathfrak{I}_\mathrm{I}$ with boundary $\Gamma_\alpha \subset \mathbb{R}^1$. Unit vector $\mathbf{n}_\alpha$ is normal to Γ_α and oriented to be outward positive from and tangent to Ω_α. Unit vector $\mathbf{n}_\beta$ is normal to Ω_α and positive outward from phase β on one side of the interface while unit vector $\mathbf{n}_\gamma$ is also normal to Ω_α but is positive outward from phase γ on the other side of the interface such that at any point on the surface, $\mathbf{n}_\beta \cdot \mathbf{n}_\gamma = -1$

$$-\int\limits_{\Gamma_\alpha} \mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{n}_\alpha \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha} G_{\Omega i\alpha} \, \mathrm{d}\mathfrak{r} = 0, \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I} \,. \tag{2.53}$$

This equation is notationally identical and conceptually similar to the corresponding equation for a phase, Eq. (2.8), with the differences being that the surface domain is two-dimensional, the boundary is one-dimensional, and all densities are per unit area rather than per unit volume.

The conversion of Eq. (2.53) for an interface to the form that applies at a point within the interface requires that the integrals over Γ_α be transformed to integrals over Ω_α. Part of this task can be accomplished making use of the surface transport theorem [8]:

Theorem 2.3 (T[2,(0,0),2]) *For a smooth continuous and differentiable function f defined over a domain $\Omega_\alpha \subset \mathbb{R}^2$ that may deform with time t due to velocity $\mathbf{w}_\alpha$ of the domain and of its closed boundary, Γ_α, designate the normal to Ω_α as $\mathbf{n}_\beta$, the normal to Γ_α that is tangent to Ω_α as $\mathbf{n}_\alpha$, and define the unit tensor $\mathsf{I}'_\alpha = \mathsf{I} - \mathbf{n}_\beta \mathbf{n}_\beta$. Then,*

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Omega_\alpha(t)} f \, \mathrm{d}\mathfrak{r} = \int\limits_{\Omega_\alpha(t)} \frac{\partial' f}{\partial t} \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha(t)} f \mathbf{w}_\alpha \cdot \left(\nabla' \cdot \mathsf{I}'_\alpha \right) \mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_\alpha(t)} f \mathbf{w}_\alpha \cdot \mathbf{n}_\alpha \, \mathrm{d}\mathfrak{r} \,, \tag{2.54}$$

where the partial derivative with respect to time for a point fixed to Ω_α is defined as

$$\frac{\partial'}{\partial t} = \frac{\mathrm{d}}{\mathrm{d}t} - \mathbf{w}_\alpha \cdot \nabla' \; ; \tag{2.55}$$

and $\nabla' \cdot$ *and* ∇' *are the surface divergence and surface gradient operators, respectively, defined as*

$$\nabla' \cdot = \left(\mathsf{l}'_\alpha \cdot \nabla \right) \cdot \tag{2.56}$$

and

$$\nabla' = \mathsf{l}'_\alpha \cdot \nabla \; . \tag{2.57}$$

Note that l'_α is the unit tensor in the surface α (i.e., in diagonal form, the entries on the diagonal associated with tangential directions in the surface are both 1, while the component associated with the normal direction is zero). When f is the density of a conserved quantity and Ω_α is an interface between phases, the left side of Eq. (2.54) is the change in the total amount of the conserved quantity with time over the interfacial area. The three terms on the right side of Eq. (2.54) contribute to this change, respectively, due to the change in f at a point fixed on the surface, due to expansion of the size of the surface because of deformation of its shape, and due to changes in the size of the surface due to movement of the boundary curve.

Also of use in transforming the general conservation equation is the surface divergence theorem [8]:

Theorem 2.4 (D[2,(0,0),2]) *For a smooth continuous and differentiable tensor function* $\mathbf{f}$ *defined over a domain* $\Omega_\alpha \subset I\!R^2$ *that may deform with time* t *due to velocity* $\mathbf{w}_\alpha$ *of the domain and of its closed boundary,* Γ_α*, designate the normal to* Ω_α *as* $\mathbf{n}_\beta$*, the normal to* Γ_α *that is tangent to* Ω_α *as* $\mathbf{n}_\alpha$*, and define the unit tensor* $\mathsf{l}'_\alpha = \mathsf{l} - \mathbf{n}_\beta \mathbf{n}_\beta$*. Then,*

$$\int_{\Omega_\alpha(t)} \operatorname{div}' \mathbf{f} \, \mathrm{d}\mathfrak{r} = - \int_{\Omega_\alpha(t)} \mathbf{f} \cdot \left(\nabla' \cdot \mathsf{l}'_\alpha \right) \mathrm{d}\mathfrak{r} + \int_{\Gamma_\alpha(t)} \mathbf{f} \cdot \mathbf{n}_\alpha \, \mathrm{d}\mathfrak{r} \; , \tag{2.58}$$

where div′ *is the surface divergence operator that contracts the last index of* $\mathbf{f}$ *and* $\nabla' \cdot$ *is the surface divergence operator defined as*

$$\nabla' \cdot = \left(\mathsf{l}'_\alpha \cdot \nabla \right) \cdot \; . \tag{2.59}$$

Because

$$\nabla' \cdot \mathsf{l}'_\alpha = - \left(\nabla' \cdot \mathbf{n}_\beta \right) \mathbf{n}_\beta \; , \tag{2.60}$$

Equation (2.58) can be written as

$$\int_{\Omega_\alpha(t)} \left[\operatorname{div}' \mathbf{f} - \left(\nabla' \cdot \mathbf{n}_\beta \right) \mathbf{f} \cdot \mathbf{n}_\beta \right] \mathrm{d}\mathfrak{r} = \int_{\Gamma_\alpha(t)} \mathbf{f} \cdot \mathbf{n}_\alpha \, \mathrm{d}\mathfrak{r} \; . \tag{2.61}$$

Application of the product rule to the second term gives

$$\int_{\Omega_\alpha(t)} \operatorname{div}' \left(\mathbf{f} - \mathbf{f} \cdot \mathbf{n}_\beta \mathbf{n}_\beta \right) \mathrm{d}\mathfrak{r} = \int_{\Gamma_\alpha(t)} \mathbf{f} \cdot \mathbf{n}_\alpha \, \mathrm{d}\mathfrak{r} \; . \tag{2.62}$$

However,

$$\mathbf{f} - \mathbf{f}\cdot\mathbf{n}_\beta\mathbf{n}_\beta = \mathbf{f}\cdot\left(\mathsf{I} - \mathbf{n}_\beta\mathbf{n}_\beta\right) = \mathbf{f}\cdot\mathsf{I}'_\alpha \,. \tag{2.63}$$

Substitution of Eq. (2.63) into Eq. (2.62), provides an alternative, but equivalent, form of D[2,(0,0),2] as:

$$\int\limits_{\Omega_\alpha(t)} \mathrm{div}'\left(\mathbf{f}\cdot\mathsf{I}'_\alpha\right)\,\mathrm{d}\mathfrak{r} = \int\limits_{\Gamma_\alpha(t)} \mathbf{f}\cdot\mathbf{n}_\alpha\,\mathrm{d}\mathfrak{r} \,. \tag{2.64}$$

With f replaced by $F_{i\alpha}$ in transport theorem Eq. (2.54), $\mathbf{f}$ replaced by $F_{i\alpha}\mathbf{v}_{i\alpha}$ in divergence theorem Eq. (2.58), and $\mathbf{f}$ replaced by $\mathbf{S}_{\Gamma i\alpha}$ in alternative divergence theorem Eq. (2.64), relations are obtained that allow the boundary integrals to be eliminated from Eq. (2.53). The result is the following:

$$\begin{aligned}&\int\limits_{\Omega_\alpha}\left[\frac{\partial' F_{i\alpha}}{\partial t} + \nabla'\cdot\left(\mathbf{v}_{i\alpha}F_{i\alpha}\right) + F_{i\alpha}\left(\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha\right)\cdot\left(\nabla'\cdot\mathsf{I}'_\alpha\right)\right]\mathrm{d}\mathfrak{r}\\ &\quad - \int\limits_{\Omega_\alpha}\left[S_{\Omega T i\alpha} + \mathrm{div}'\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathsf{I}'_\alpha\right) + G_{\Omega i\alpha}\right]\mathrm{d}\mathfrak{r} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I} \,.\end{aligned} \tag{2.65}$$

In this equation, $\left(\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha\right)\cdot\left(\nabla'\cdot\mathsf{I}'_\alpha\right) = 0$ because this quantity is the difference between the species velocity and the interface velocity in the direction normal to the surface multiplied by the surface curvature. As discussed previously, this velocity difference is zero. Also the total body source is composed of two components. The first is due to external sources acting on the entity. The second is due to the fact that at every point within the surface, an adjacent phase can impact the properties of the surface. Thus, fluxes from a phase to an interface at a point are treated as part of the body source. To make this explicit, we break the body source into these two components according to

$$S_{\Omega T i\alpha} = S_{\Omega i\alpha} + \sum_{\kappa\in\mathfrak{I}^+_{c\alpha}} \sum_{j\in\mathfrak{I}_s} \underset{j\kappa\to i\alpha}{X} \,, \tag{2.66}$$

where $\mathfrak{I}^+_{c\alpha}$ is the connected set for interface α that is of higher dimensionality (i.e., phases in the connected set), and $\underset{j\kappa\to i\alpha}{X}$ is the body source component due to transfer of the property being conserved from species j in entity κ to species i in entity α. Because the extent of the surface domain, Ω_α, is arbitrary, the integrand in Eq. (2.65) must be zero at every microscale point, not just when integrated over the domain. Application of these conditions provides the general microscale point form of the surface conservation equation,

$$\begin{aligned}&\frac{\partial' F_{i\alpha}}{\partial t} + \nabla'\cdot\left(\mathbf{v}_{i\alpha}F_{i\alpha}\right) - S_{\Omega i\alpha} - \sum_{\kappa\in\mathfrak{I}^+_{c\alpha}} \sum_{j\in\mathfrak{I}_s} \underset{j\kappa\to i\alpha}{X} - \mathrm{div}'\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathsf{I}'_\alpha\right) - G_{\Omega i\alpha} = 0\\ &\qquad\qquad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I} \,.\end{aligned} \tag{2.67}$$

This equation may also be written in terms of the material derivative as

$$\frac{\mathrm{D}_{i\alpha}F_{i\alpha}}{\mathrm{D}t}+F_{i\alpha}\mathbf{l}'_{\alpha}{:}\mathbf{d}'_{i\alpha}-S_{\Omega i\alpha}-\sum_{\kappa\in\mathfrak{I}^{+}_{c\alpha}}\sum_{j\in\mathfrak{I}_{s}}\underset{j\kappa\to i\alpha}{X}-\mathrm{div}'\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathbf{l}'_{\alpha}\right)-G_{\Omega i\alpha}=0$$

$$\text{for } i\in\mathfrak{I}_{s},\alpha\in\mathfrak{I}_{\mathrm{I}}\,, \tag{2.68}$$

where

$$\frac{\mathrm{D}_{i\alpha}}{\mathrm{D}t}=\frac{\partial'}{\partial t}+\mathbf{v}_{i\alpha}\cdot\nabla' \tag{2.69}$$

and

$$\mathbf{d}'_{i\alpha}=\left[\nabla'\mathbf{v}_{i\alpha}+\left(\nabla'\mathbf{v}_{i\alpha}\right)^{\mathrm{T}}\right]\,. \tag{2.70}$$

The general microscale conservation equation given as Eq. (2.67) is a more convenient form to work with than Eq. (2.68) for deriving larger scale equations because of the forms of the theorems used to affect the change. Considerations for changing the species equations indicated to forms that apply for a surface entity as a whole are the same as those discussed in the first full paragraph following Eq. (2.16). In the following section, we will provide the specific conservation and balance equations for interfaces. Note that, although the appearance of the general forms for the surface and phase equations as given by Eqs. (2.67) and (2.13) are quite similar, the contributions to specific body source terms will be seen to be very different because of the transfer from adjacent phases to the interface.

2.4.2 Specific Conservation and Balance Principles

Specific conservation and balance equations can be stated by proper identification of the variables that appear in Eq. (2.67) or its equivalent version, Eq. (2.68). Here a full set of microscale conservation and balance equations for an interface is provided. This is accomplished in a manner similar to that employed with phases in Sect. 2.3.2.

The prime conceptual extension required for interfaces in comparison to phases is related to the fact that transfer of a property at the boundary of a phase is with the domain of an interface. Therefore, processes that are accounted for as boundary conditions for phase equations are parts of the body source terms for interface equations. These additional terms are related to advective and non-advective boundary sources for the phases that are body sources for the interface. The domain of an α interface, Ω_{α}, is the boundary of two phases on each side of the interface. Note that an interface is defined such that it is the boundary between a particular pair of phases; a different pair of phases is separated by a different interface. Also, if a third phase is present, the interface may have an edge boundary that is a common curve. At the microscale, we will only be interested in members of the connected set that are of higher order dimensionality than the entity of interest. Thus if the two phases that bound interface α are designated as β and γ, we can define the set of phase

Table 2.3 Physical variables for species-based interface equations in partial derivative or material form. $\mathcal{M}_{i\alpha}$, $\mathcal{P}_{i\alpha}$, $\mathcal{E}_{i\alpha}$, $\mathcal{S}_{i\alpha}$, and $\mathcal{G}_{i\alpha}$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential for species i in interface α

$$\mathcal{F}_{i\alpha} = \frac{\partial' F_{i\alpha}}{\partial t} + \nabla' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^{+}} \sum_{j \in \mathcal{J}_s} \underset{j\kappa \to i\alpha}{X} - \mathrm{div}' \left(\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}'_{\alpha} \right) - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_{\mathrm{I}}$$

$$\mathcal{F}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha} F_{i\alpha}}{\mathrm{D}t} + F_{i\alpha} \mathbf{l}'_{\alpha} : \mathbf{d}'_{i\alpha} - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^{+}} \sum_{j \in \mathcal{J}_s} \underset{j\kappa \to i\alpha}{X} - \mathrm{div}' \left(\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}'_{\alpha} \right) - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_{\mathrm{I}}$$

$\mathcal{F}_{i\alpha}$	$F_{i\alpha}$	$S_{\Omega i\alpha}$	$\underset{j\kappa\to i\alpha}{X}$	$\mathbf{S}_{\Gamma i\alpha}$	$G_{\Omega i\alpha}$
$\mathcal{M}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha}$	—	$\delta_{ij} \underset{i\kappa\to i\alpha}{M}$	—	$r_{i\alpha}$
$\mathcal{P}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha}$	$\delta_{ij} \mathbf{v}_{i\kappa} \underset{i\kappa\to i\alpha}{M} + \underset{j\kappa\to i\alpha}{\mathbf{T}}$	$\mathbf{t}_{i\alpha}$	$\mathbf{p}_{i\alpha} + r_{i\alpha} \mathbf{v}_{i\alpha}$
$\mathcal{E}_{i\alpha}$	$E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2}$	$\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$ $+h_{i\alpha}$	$\delta_{ij} \left(\frac{E_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} + \frac{\mathbf{v}_{i\kappa} \cdot \mathbf{v}_{i\kappa}}{2} \right) \underset{i\kappa\to i\alpha}{M}$ $+\mathbf{v}_{j\kappa} \cdot \underset{j\kappa\to i\alpha}{\mathbf{T}} + \underset{j\kappa\to i\alpha}{Q}$	$\mathbf{t}_{i\alpha}{}^{\mathrm{T}} \cdot \mathbf{v}_{i\alpha}$ $+\mathbf{q}_{i\alpha}$	$e_{i\alpha} + \mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$ $+r_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2}$
$\mathcal{S}_{i\alpha} - \Lambda_{i\alpha}$	$\eta_{i\alpha}$	$b_{i\alpha}$	$\delta_{ij} \frac{\eta_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} \underset{i\kappa\to i\alpha}{M} + \underset{j\kappa\to i\alpha}{\Phi}$	$\boldsymbol{\varphi}_{i\alpha}$	$\Lambda_{i\alpha}$
$\mathcal{G}_{i\alpha}$	$\Psi_{i\alpha}$	$-\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$	$\delta_{ij} \underset{i\kappa\to i\alpha}{M} \psi_{i\alpha}$	—	$\rho_\alpha \omega_{i\alpha} \left[\frac{\partial' \psi_{i\alpha}}{\partial t} \right.$ $\left. +\mathbf{g}_{i\alpha} \cdot \left(\mathbf{I} - \mathbf{l}'_{\alpha} \right) \cdot \mathbf{v}_{i\alpha} \right]$ $+r_{i\alpha} \psi_{i\alpha}$

Inter-entity Exchange Terms

$$\underset{i\kappa\to i\alpha}{M} = \mathbf{n}_\kappa \cdot \left[\rho_\kappa \omega_{i\kappa} \left(\mathbf{v}_{i\kappa} - \mathbf{v}_\alpha \right) \right] \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^{+}$$

$$\underset{j\kappa\to i\alpha}{\mathbf{T}} = - \underset{j\kappa\to i\alpha}{z_T} \mathbf{t}_{j\kappa} \cdot \mathbf{n}_\kappa \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^{+}$$

$$\underset{j\kappa\to i\alpha}{Q} = - \underset{j\kappa\to i\alpha}{z_Q} \mathbf{q}_{j\kappa} \cdot \mathbf{n}_\kappa \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^{+}$$

$$\underset{j\kappa\to i\alpha}{\Phi} = - \underset{j\kappa\to i\alpha}{z_\Phi} \boldsymbol{\varphi}_{j\kappa} \cdot \mathbf{n}_\kappa \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^{+}$$

entities bounded by interface α as the connected set $\mathcal{J}_{c\alpha} \cap \mathcal{J}_{\mathrm{P}} = \{\beta, \gamma\}$, where $\mathcal{J}_{c\alpha}$ is the connected set of phases and common curves to interface α and $\mathcal{J}_{\mathrm{P}}$ is the index set of phases in the system. A simpler notation can be employed by denoting the connected set of higher order that bounds an entity as $\mathcal{J}_{c\alpha}^{+}$ and one of lower order as $\mathcal{J}_{c\alpha}^{-}$. Thus, if α refers to an interface, $\mathcal{J}_{c\alpha} \cap \mathcal{J}_{\mathrm{P}} = \mathcal{J}_{c\alpha}^{+}$ is the set of phases connected to the interface and $\mathcal{J}_{c\alpha} \cap \mathcal{J}_{\mathrm{C}} = \mathcal{J}_{c\alpha}^{-}$ is the set of common curves bounding the interface. We note also that $\mathcal{J}_{c\alpha}^{+} \cup \mathcal{J}_{c\alpha}^{-} = \mathcal{J}_{c\alpha}$.

Specific forms of conservation and balance equations for properties of a chemical species in an interface are given in Table 2.3. Summation of a particular conservation or balance equation over all species in the interface results in the equations provided in Table 2.4. We will examine these equations in some detail and also indicate the relation between interface-based variables and species-based variables.

The point form of the microscale mass conservation equation for a chemical species i in an interface α is obtained from Table 2.3 based on the variables included in row $\mathcal{M}_{i\alpha}$. Substitution of these variables into Eq. (2.67), which is also the

Table 2.4 Physical variables for entity-based interface equations in partial derivative or material form. $\mathcal{M}_\alpha$, $\mathcal{P}_\alpha$, $\mathcal{E}_\alpha$, $\mathcal{S}_\alpha$, and $\mathcal{G}_\alpha$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential in interface α

$$\mathcal{F}_\alpha = \frac{\partial' F_\alpha}{\partial t} + \nabla' \cdot (\mathbf{v}_\alpha F_\alpha) - S_{\Omega\alpha} - \sum_{\kappa \in \mathfrak{I}_{c\alpha}^+} \underset{\kappa\to\alpha}{X} - \mathrm{div}'\left(\mathbf{S}_{\Gamma\alpha} \cdot \mathbf{l}'_\alpha\right) - G_{\Omega\alpha} = 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I}$$

$$\mathcal{F}_{*\alpha} = \frac{\mathrm{D}_\alpha F_\alpha}{\mathrm{D}t} + F_\alpha \mathbf{l}'_\alpha{:}\mathbf{d}'_\alpha - S_{\Omega\alpha} - \sum_{\kappa \in \mathfrak{I}_{c\alpha}^+} \underset{\kappa\to\alpha}{X} - \mathrm{div}'\left(\mathbf{S}_{\Gamma\alpha} \cdot \mathbf{l}'_\alpha\right) - G_{\Omega\alpha} = 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I}$$

$\mathcal{F}_\alpha$	F_α	$S_{\Omega\alpha}$	$\underset{\kappa\to\alpha}{X}$	$\mathbf{S}_{\Gamma\alpha}$	$G_{\Omega i\alpha}$
$\mathcal{M}_\alpha$	ρ_α	—	$\underset{\kappa\to\alpha}{M}$	—	—
$\mathcal{P}_\alpha$	$\rho_\alpha \mathbf{v}_\alpha$	$\rho_\alpha \mathbf{g}_\alpha$	$\mathbf{v}_\kappa \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\mathbf{T}}$	$\mathbf{t}_\alpha$	—
$\mathcal{E}_\alpha$	E_α $+\rho_\alpha \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2}$ $+\rho_\alpha K_{E\alpha}$	$\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha$ $+h_\alpha$ $+\sum_{i \in \mathfrak{I}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}'_\alpha \cdot \mathbf{u}_{i\alpha}$	$\left(\frac{E_\kappa}{\rho_\kappa} + \frac{\mathbf{v}_\kappa \cdot \mathbf{v}_\kappa}{2} + K_{E\kappa}\right) \underset{\kappa\to\alpha}{M}$ $+\mathbf{v}_\kappa \cdot \underset{\kappa\to\alpha}{\mathbf{T}} + \underset{\kappa\to\alpha}{Q}$	$\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha$	—
$\mathcal{S}_\alpha - \Lambda_\alpha$	η_α	b_α	$\frac{\eta_\kappa}{\rho_\kappa} \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\Phi}$	$\boldsymbol{\varphi}_\alpha$	Λ_α
$\mathcal{G}_\alpha$	Ψ_α	$-\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha$ $-\sum_{i \in \mathfrak{I}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}'_\alpha \cdot \mathbf{u}_{i\alpha}$	$+\sum_{i \in \mathfrak{I}_s} \sum_{\kappa \in \mathfrak{I}_{c\alpha}^+} \underset{i\kappa\to i\alpha}{M} \psi_{i\alpha}$	$-\sum_{i \in \mathfrak{I}_s} \rho_\alpha \omega_{i\alpha} \psi_{i\alpha} \mathbf{u}_{i\alpha}$	$\sum_{i \in \mathfrak{I}_s} \rho_\alpha \omega_{i\alpha} \left[\frac{\partial' \psi_{i\alpha}}{\partial t}\right.$ $\left. + \mathbf{g}_{i\alpha} \cdot \left(\mathbf{I} - \mathbf{l}'_\alpha\right) \cdot \mathbf{v}_{i\alpha}\right]$ $+\sum_{i \in \mathfrak{I}_s} r_{i\alpha} \psi_{i\alpha}$

Inter-entity Exchange Terms

$$\underset{\kappa\to\alpha}{M} = \sum_{i \in \mathfrak{I}_s} \underset{i\kappa\to i\alpha}{M} \quad \text{for } \kappa \in \mathfrak{I}_{c\alpha}^+$$

$$\underset{\kappa\to\alpha}{\mathbf{T}} = \sum_{j \in \mathfrak{I}_s} \sum_{i \in \mathfrak{I}_s} \left[\underset{j\kappa\to i\alpha}{\mathbf{T}} + \delta_{ij} (\mathbf{v}_{i\kappa} - \mathbf{v}_\kappa) \underset{i\kappa\to i\alpha}{M}\right] \quad \text{for } \kappa \in \mathfrak{I}_{c\alpha}^+$$

$$\underset{\kappa\to\alpha}{Q} = \sum_{j \in \mathfrak{I}_s} \sum_{i \in \mathfrak{I}_s} \left\{\underset{j\kappa\to i\alpha}{Q} + (\mathbf{v}_{j\kappa} - \mathbf{v}_\kappa) \cdot \underset{j\kappa\to i\alpha}{\mathbf{T}} + \delta_{ij} \left[\frac{E_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} + \frac{\mathbf{u}_{i\kappa} \cdot \mathbf{u}_{i\kappa}}{2} - \left(\frac{E_\kappa}{\rho_\kappa} + K_{E\kappa}\right)\right] \underset{i\kappa\to i\alpha}{M}\right\} \quad \text{for } \kappa \in \mathfrak{I}_{c\alpha}^+$$

$$\underset{\kappa\to\alpha}{\Phi} = \sum_{j \in \mathfrak{I}_s} \sum_{i \in \mathfrak{I}_s} \left\{\underset{j\kappa\to i\alpha}{\Phi} + \delta_{ij} \left[\frac{\eta_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} - \frac{\eta_\kappa}{\rho_\kappa}\right] \underset{i\kappa\to i\alpha}{M}\right\} \quad \text{for } \kappa \in \mathfrak{I}_{c\alpha}^+$$

equation at the top of the table, yields

$$\mathcal{M}_{i\alpha} = \frac{\partial'(\rho_\alpha \omega_{i\alpha})}{\partial t} + \nabla' \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}) - \sum_{\kappa \in \mathfrak{I}_{c\alpha}^+} \underset{i\kappa\to i\alpha}{M} - r_{i\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I}\,, \tag{2.71}$$

where ρ_α is the mass per area, $\omega_{i\alpha}$ is the mass fraction of species i, $\mathbf{v}_{i\alpha}$ is the velocity of species i (which, in the normal direction to the interface, is equal to the interface velocity), $\underset{i\kappa\to i\alpha}{M}$ is an effective body source for the species i in the interface due to transfer of i from the phases within $\mathfrak{I}_{c\alpha}^+$ to interface α, and $r_{i\alpha}$ is the rate of generation of species i in interface α due to any and all chemical reactions within the interface. This equation is very similar to the mass conservation equation for a species in a phase given as Eq. (2.17). The differences are: the time derivative is at a fixed point in a surface rather than in a phase; the divergence term models outward flux in the surface rather than in three-dimensions; and there is a new term, $\underset{i\kappa\to i\alpha}{M}$. In the bottom portion of Table 2.3, the explicit form of $\underset{i\kappa\to i\alpha}{M}$ is given in terms of the properties of the phases at the interface. Note that κ takes on the index values of the two phases adjacent to the α interface.

The point form of the total mass conservation equation is most directly obtained by substituting the variables in the $\mathcal{M}_\alpha$ row of Table 2.4 into the equation at the top of the table. The result is

$$\mathcal{M}_\alpha = \frac{\partial' \rho_\alpha}{\partial t} + \nabla' \cdot (\rho_\alpha \mathbf{v}_\alpha) - \sum_{\kappa \in \mathfrak{I}_{c\alpha}^+} \underset{\kappa\to\alpha}{M} = 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I} \,. \tag{2.72}$$

Equation (2.72) can be obtained directly by summing Eq. (2.71) over all chemical species if one makes use of the definition of the barycentric velocity as given by Eq. (2.23) for the interface as well as for the adjacent phases. Also, the traditional jump conditions for mass exchange between phases can be obtained when the interface is considered massless such that ρ_α and $r_{i\alpha}$ are both zero. The species-based jump condition is the statement that the summation in Eq. (2.71) is equal to zero. For the interface entity as a whole, the condition is that the summation in Eq. (2.72) is zero. On a physical basis, both of these jump conditions state that at a point at the boundary of a phase where material leaves that phase, it immediately enters the adjacent phase. The more general mass conservation equations for the interface additionally allow for material to stay in the interface, move in the interfacial surface, and participate in chemical reactions.

The microscale conservation of momentum equations for a species in an interface and for all species in the interface entity as a whole can be obtained, respectively, from Tables 2.3 and 2.4 as

$$\begin{aligned}\mathcal{P}_{i\alpha} &= \frac{\partial'(\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha})}{\partial t} + \nabla' \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \mathbf{v}_{i\alpha}) - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \\ &\quad - \sum_{\kappa \in \mathfrak{I}_{c\alpha}^+} \sum_{j \in \mathfrak{I}_s} \left(\delta_{ij} \mathbf{v}_{i\kappa} \underset{i\kappa\to i\alpha}{M} + \underset{j\kappa\to i\alpha}{\mathbf{T}} \right) \\ &\quad - \nabla' \cdot \left(\mathbf{l}'_\alpha \cdot \mathbf{t}_{i\alpha}{}^\mathrm{T} \right) - \mathbf{p}_{i\alpha} - r_{i\alpha} \mathbf{v}_{i\alpha} = \mathbf{0} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I}\end{aligned} \tag{2.73}$$

and

$$\begin{aligned}\mathcal{P}_\alpha &= \frac{\partial'(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \nabla' \cdot (\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha) - \rho_\alpha \mathbf{g}_\alpha \\ &\quad - \sum_{\kappa \in \mathfrak{I}_{c\alpha}^+} \left(\mathbf{v}_\kappa \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\mathbf{T}} \right) - \nabla' \cdot \left(\mathbf{l}'_\alpha \cdot \mathbf{t}_\alpha \right) = \mathbf{0} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I} \,.\end{aligned} \tag{2.74}$$

The notation employed should be clear based on discussions of the phase equations, although there are two additional elements. The quantity δ_{ij} in Eq. (2.73) is the Kronecker delta, equal to 1 when $i = j$ and zero otherwise. This is necessary because the term it multiplies is momentum transfer between a bounding phase and the interface that accompanies mass exchange between these entities. Thus, only when species i in the phase $\kappa \in \mathfrak{I}_{c\alpha}^{+}$ is involved in inter-entity mass transfer will that impact the momentum of species i in the interface. On the other hand, stress effects can be exerted by a species in a phase on a different species in the interface. The quantity $\underset{j\kappa\to i\alpha}{z_T}$ introduced in the definition of $\underset{j\kappa\to i\alpha}{\mathbf{T}}$ at the bottom of Table 2.3 is the fraction of stress tensor $\mathbf{t}_{j\kappa}$ (i.e., the stress associated with species j in phase κ) that is exerted on species i in interface α. Thus, $\underset{j\kappa\to i\alpha}{z_T}$ will satisfy the condition

$$\sum_{i\in\mathfrak{I}_s} \underset{j\kappa\to i\alpha}{z_T} = 1 \quad \text{for}\, j \in \mathfrak{I}_s, \kappa \in \mathfrak{I}_{c\alpha}^{+}, \alpha \in \mathfrak{I}_{\mathrm{I}} \,. \tag{2.75}$$

We note also that the surface entity-based stress tensor, $\mathbf{t}_\alpha$, is defined in terms of the surface species-based stress tensor exactly as in Eq. (2.30) for a phase.

For the situation where the interface is massless, full momentum equations for a species and for an entity simplify to jump conditions for the momentum of the species and of the phase entity, respectively, as

$$-\sum_{\kappa\in\mathfrak{I}_{c\alpha}^{+}} \sum_{j\in\mathfrak{I}_s} \mathbf{n}_\kappa\cdot \left[\delta_{ij}\rho_\kappa\omega_{i\kappa}\left(\mathbf{v}_{i\kappa}-\mathbf{v}_\alpha\right)\mathbf{v}_{i\kappa} - \underset{j\kappa\to i\alpha}{z_T}\,\mathbf{t}_{j\kappa}{}^{\mathrm{T}}\right] - \nabla'\cdot\left(\mathbf{l}'_\alpha\cdot\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\right) = \mathbf{0}$$

$$\text{for}\; i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{I}} \tag{2.76}$$

and

$$-\sum_{\kappa\in\mathfrak{I}_{c\alpha}^{+}} \mathbf{n}_\kappa\cdot\left[\rho_\kappa\left(\mathbf{v}_\kappa-\mathbf{v}_\alpha\right)\mathbf{v}_\kappa - \mathbf{t}_\kappa\right] - \nabla'\cdot\left(\mathbf{l}'_\alpha\cdot\mathbf{t}_\alpha\right) = \mathbf{0} \quad \text{for}\; \alpha \in \mathfrak{I}_{\mathrm{I}}\,, \tag{2.77}$$

where the expression for the exchange of momentum between the interface and the adjacent phases has been substituted into the momentum equation; and terms containing ρ_α for $\alpha \in \mathfrak{I}_{\mathrm{I}}$ have been dropped because the interface is massless. In practice, the most commonly employed form of the microscale momentum jump condition is Eq. (2.77) with the divergence term dropped when interfacial tension effects are unimportant. In subsequent chapters, the full dynamic equations will be employed.

The species-based conservation of energy equation for an interface can be written, based on the entries in Table 2.3, as

$$\begin{aligned}\mathcal{E}_{i\alpha} = {} & \frac{\partial'}{\partial t}\left(E_{i\alpha}+\rho_\alpha\omega_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right) + \nabla'\cdot\left[\left(E_{i\alpha}+\rho_\alpha\omega_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right)\mathbf{v}_{i\alpha}\right] \\ & -\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha} - h_{i\alpha} \\ & -\sum_{\kappa\in\mathfrak{I}_{c\alpha}^{+}}\sum_{j\in\mathfrak{I}_s}\left[\delta_{ij}\left(\frac{E_{i\kappa}}{\rho_\kappa\omega_{i\kappa}}+\frac{\mathbf{v}_{i\kappa}\cdot\mathbf{v}_{i\kappa}}{2}\right)\underset{i\kappa\to i\alpha}{M} + \mathbf{v}_{j\kappa}\cdot\underset{j\kappa\to i\alpha}{\mathbf{T}} + \underset{j\kappa\to i\alpha}{Q}\right]\end{aligned}$$

$$\begin{aligned}
&-\nabla'\cdot\left[\mathsf{l}'_\alpha\cdot\left(\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\cdot\mathbf{v}_{i\alpha}+\mathbf{q}_{i\alpha}\right)\right]\\
&-e_{i\alpha}-\mathbf{p}_{i\alpha}\cdot\mathbf{v}_{i\alpha}-r_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}=0\quad\text{for } i\in\mathfrak{I}_s,\alpha\in\mathfrak{I}_{\mathrm{I}}\,.
\end{aligned}\tag{2.78}$$

The conservation of energy equation for an interface as a whole is

$$\begin{aligned}
\mathcal{E}_\alpha=&\frac{\partial'}{\partial t}\left[E_\alpha+\rho_\alpha\left(\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}+K_{E\alpha}\right)\right]+\nabla'\cdot\left\{\left[E_\alpha+\rho_\alpha\left(\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}+K_{E\alpha}\right)\right]\mathbf{v}_\alpha\right\}\\
&-\rho_\alpha\mathbf{g}_\alpha\cdot\mathbf{v}_\alpha-\sum_{i\in\mathfrak{I}_s}\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathsf{l}'_\alpha\cdot\mathbf{u}_{i\alpha}-h_\alpha\\
&-\sum_{\kappa\in\mathfrak{I}^+_{c\alpha}}\left[\left(\frac{E_\kappa}{\rho_\kappa}+\frac{\mathbf{v}_\kappa\cdot\mathbf{v}_\kappa}{2}+K_{E\kappa}\right)\underset{\kappa\to\alpha}{M}+\mathbf{v}_\kappa\cdot\underset{\kappa\to\alpha}{\mathbf{T}}+\underset{\kappa\to\alpha}{Q}\right]\\
&-\nabla'\cdot\left[\mathsf{l}'_\alpha\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha\right)\right]=0\quad\text{for } \alpha\in\mathfrak{I}_{\mathrm{I}}\,.
\end{aligned}\tag{2.79}$$

The definition of $\underset{j\kappa\to i\alpha}{Q}$ in Eq. (2.78) provided at the end of Table 2.3 makes use of the parameter $\underset{j\kappa\to i\alpha}{z_Q}$. The purpose of this parameter is to account for the fact that contributions to heat conduction from phase κ due to species j can be to species i in interface entity α. This parameter, or actually set of parameters with the range of indices, satisfies the condition

$$\sum_{i\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{z_Q}=1\quad\text{for } j\in\mathfrak{I}_s,\kappa\in\mathfrak{I}^+_{c\alpha},\alpha\in\mathfrak{I}_{\mathrm{I}}\,.\tag{2.80}$$

Note that Eq. (2.79) may also be obtained directly as the sum of Eq. (2.78) over all species i in interface entity α. This is left as an exercise.

The energy jump condition between phases that is usually employed is obtained by dropping all the terms except for the summations over $\mathfrak{I}^+_{c\alpha}$ in Eq. (2.78) or Eq. (2.79). This simplification is appropriate under conditions where the mass density of the interface, ρ_α, is negligible, the rates of change and the surficial fluxes of the internal energy of the interface are small, the body sources of energy due to processes such as radiation are negligible, and the work and heat transfer due to movement in the surface is negligible. The statement that a term is “negligible” or “small” is relative to the advective and non-advective fluxes of energy to the interface from the adjacent phases.

The balance of entropy equation for a species in an interface can be assembled from Table 2.3 as

$$\begin{aligned}
\mathcal{S}_{i\alpha}=&\frac{\partial'\eta_{i\alpha}}{\partial t}+\nabla'\cdot\left(\eta_{i\alpha}\mathbf{v}_{i\alpha}\right)-b_{i\alpha}-\sum_{\kappa\in\mathfrak{I}^+_{c\alpha}}\sum_{j\in\mathfrak{I}_s}\left(\delta_{ij}\frac{\eta_{i\kappa}}{\rho_\kappa\omega_{i\kappa}}\underset{i\kappa\to i\alpha}{M}+\underset{j\kappa\to i\alpha}{\Phi}\right)\\
&-\nabla'\cdot\left(\mathsf{l}'_\alpha\cdot\boldsymbol{\varphi}_{i\alpha}\right)=\Lambda_{i\alpha}\quad\text{for } i\in\mathfrak{I}_s,\alpha\in\mathfrak{I}_{\mathrm{I}}\,.
\end{aligned}\tag{2.81}$$

The overall balance of entropy equation for an interface from the entries in Table 2.4 is

$$\mathcal{S}_\alpha = \frac{\partial' \eta_\alpha}{\partial t} + \nabla' \cdot (\eta_\alpha \mathbf{v}_\alpha) - b_\alpha - \sum_{\kappa \in \mathfrak{I}^+_{c\alpha}} \left(\frac{\eta_\kappa}{\rho_\kappa} \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\Phi} \right)$$
$$- \nabla' \cdot \left(\mathbf{l}'_\alpha \cdot \boldsymbol{\varphi}_\alpha \right) = \Lambda_\alpha \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I} \,. \tag{2.82}$$

The discussion following Eq. (2.43) regarding $\Lambda_{i\alpha}$ and Λ_α for $\alpha \in \mathfrak{I}_\mathrm{P}$ applies to the preceding equations as well for $\alpha \in \mathfrak{I}_\mathrm{I}$ such that $\Lambda_\alpha \geq 0$.

The body force potential per unit area acting on species i in interface α is written analogously to Eq. (2.44) for a volume as

$$\Psi_{i\alpha} = \rho_\alpha \omega_{i\alpha} \psi_{i\alpha} \,, \tag{2.83}$$

with the corresponding expression for the material derivative,

$$\mathcal{T}_{\mathcal{G}*i\alpha} = \frac{\mathrm{D}_{i\alpha} \Psi_{i\alpha}}{\mathrm{D}t} - \psi_{i\alpha} \frac{\mathrm{D}_{i\alpha}(\rho_\alpha \omega_{i\alpha})}{\mathrm{D}t} - \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}_{i\alpha} \psi_{i\alpha}}{\mathrm{D}t} = 0 \,. \tag{2.84}$$

The potential for the surface entity as a unit, Ψ_α, is defined as in Eq. (2.47); its material derivative is as in Eq. (2.48). Recall that for the surface expressions ρ_α is mass per area while for the phases, ρ_α is mass per volume.

The rate of change of the body force potential acting on an interface is conveniently written in terms of surface differential operators. Use of mass conservation $\mathcal{M}_{*i\alpha}$ based on Table 2.3 to eliminate $\mathrm{D}_{i\alpha}(\rho_\alpha \omega_{i\alpha})/\mathrm{D}t$ from Eq. (2.84) and expansion of $\mathrm{D}_{i\alpha} \psi_{i\alpha}/\mathrm{D}t$ according to Eq. (2.69) yields

$$\frac{\mathrm{D}_{i\alpha} \Psi_{i\alpha}}{\mathrm{D}t} + \psi_{i\alpha} \left(\rho_\alpha \omega_{i\alpha} \mathbf{l}'_\alpha{:}\mathbf{d}'_{i\alpha} - r_{i\alpha} - \sum_{\kappa \in \mathfrak{I}^+_{c\alpha}} \underset{i\kappa\to i\alpha}{M} \right)$$
$$- \rho_\alpha \omega_{i\alpha} \frac{\partial' \psi_{i\alpha}}{\partial t} - \rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \cdot \nabla' \psi_{i\alpha} = 0 \,. \tag{2.85}$$

Only the surface components of the gradient of the body force potential appear in this equation. Thus, we make use of the identity

$$\nabla' \psi_{i\alpha} + \mathbf{l}'_\alpha \cdot \mathbf{g}_{i\alpha} = \mathbf{0}' \,. \tag{2.86}$$

With this relation and Eq. (2.83) employed, Eq. (2.85) becomes the microscale balance equation for the body force potential per unit area of chemical species i in interface α

$$\mathcal{G}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha} \Psi_{i\alpha}}{\mathrm{D}t} + \Psi_{i\alpha} \mathbf{l}'_\alpha{:}\mathbf{d}'_{i\alpha} + \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - \sum_{\kappa \in \mathfrak{I}^+_{c\alpha}} \underset{i\kappa\to i\alpha}{M} \psi_{i\alpha}$$
$$- \rho_\alpha \omega_{i\alpha} \frac{\partial' \psi_{i\alpha}}{\partial t} - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \left(\mathbf{l} - \mathbf{l}'_\alpha \right) \cdot \mathbf{v}_{i\alpha} - r_{i\alpha} \psi_{i\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I} \,. \tag{2.87}$$

The elements of this equation are distributed in the appropriate columns of Table 2.3.

For the interface entity, summation of $\mathcal{G}_{i\alpha}$ over all species and rearrangement to obtain $\mathcal{G}_{*\alpha}$ results in

$$\begin{aligned}\mathcal{G}_{*\alpha} = & \frac{\mathrm{D}_{\alpha}\Psi_{\alpha}}{\mathrm{D}t} + \Psi_{\alpha}\mathbf{l}'_{\alpha}{:}\mathbf{d}'_{\alpha} + \nabla'\cdot\left(\sum_{i\in\mathfrak{I}_s}\rho_{\alpha}\omega_{i\alpha}\psi_{i\alpha}\mathbf{l}'_{\alpha}\cdot\mathbf{u}_{i\alpha}\right) \\ & + \rho_{\alpha}\mathbf{g}_{\alpha}\cdot\mathbf{v}_{\alpha} + \sum_{i\in\mathfrak{I}_s}\rho_{\alpha}\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{l}'_{\alpha}\cdot\mathbf{u}_{i\alpha} - \sum_{i\in\mathfrak{I}_s}\sum_{\kappa\in\mathfrak{I}^{+}_{c\alpha}}\underset{i\kappa\rightarrow i\alpha}{M}\psi_{i\alpha} \\ & - \sum_{i\in\mathfrak{I}_s}\rho_{\alpha}\omega_{i\alpha}\frac{\partial'\psi_{i\alpha}}{\partial t} - \sum_{i\in\mathfrak{I}_s}\rho_{\alpha}\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\left(\mathbf{l}-\mathbf{l}'_{\alpha}\right)\cdot\mathbf{v}_{i\alpha} - \sum_{i\in\mathfrak{I}_s}r_{i\alpha}\psi_{i\alpha} = 0 \\ & \text{for } \alpha\in\mathfrak{I}_{\mathrm{I}}\,. \qquad (2.88)\end{aligned}$$

The contributions to this equation are provided in Table 2.4.

2.5 Conservation and Balance Principles for a Common Curve

Common curves[5] are the third type of entity of interest in the development of conservation and balance equations. Common curves are the regions in a multiphase system that exist where three phases, and also three interfaces, meet. As boundaries of two-dimensional entities, they are one-dimensional regions. Common curves occupy neither volume nor area in a system. The measure of the extent of a common curve is its length.

Common curves play a role in providing the location where mass, momentum, energy, and entropy can be exchanged among the interfaces that meet at a curve. The common curve length thus affects the amount of the exchanges and is of interest. Conventional multiphase dynamic models do not explicitly deal with common curves nor do they evolve the extent of common curve lengths with time. By formulating full conservation and balance equations for common curves, we will provide the opportunity to include common curve phase dynamics, exchanges of properties at the curve, and the length of curves present in the model. We will present the general and then particular forms of microscale species-based and entity-based conservation and balance equations for common curves.

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[5] Although these features of a system are usually referred to as common "lines", we use the designation common "curves" in recognition of the fact that these one-dimensional regions usually have non-zero curvature.

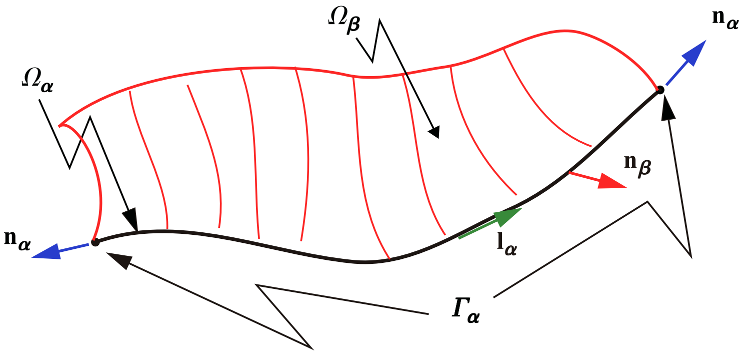

Fig. 2.3 Arbitrary curve in the region $\Omega_\alpha \subset \mathbb{R}^1$ containing common curve $\alpha \in \mathfrak{I}_\mathrm{C}$ with boundary $\Gamma_\alpha \subset \mathbb{R}^0$ consisting of the two end points of the curve. Unit vector $\mathbf{n}_\alpha$ is outward positive from and tangent to Ω_α at Γ_α. Unit vector $\mathbf{l}_\alpha$ is tangent to Ω_α. Also depicted is interface β with domain $\Omega_\beta \subset \mathbb{R}^2$ whose boundary is composed, at least partly, of Ω_α which is the curve where interface β and two other interfaces between phases meet. Unit vector $\mathbf{n}_\beta$ is normal to Ω_α and tangent to Ω_β

2.5.1 General Microscale Point Form

The procedure for development of conservation and balance equations for a common curve is almost identical to that employed in developing expressions for phases and interfaces. However, particular attention must be given to the geometry of the common curve that requires a little modification to the general conservation equation for entity properties, Eq. (2.7), or appropriate definition of variables in Eq. (2.8) for species properties.

The domain of a common curve, indicated as entity $\alpha \in \mathfrak{I}_\mathrm{C}$, that exists where three phases, indicated as β, γ, and $\delta \in \mathfrak{I}_\mathrm{P}$, meet is Ω_α such that $\Omega_\alpha = \bar{\Omega}_\beta \cap \bar{\Omega}_\gamma \cap \bar{\Omega}_\gamma$.[6] A schematic diagram of the common curve is provided in Fig. 2.3. The fact that Ω_α is a curve means that $\Omega_\alpha \subset \mathbb{R}^1$. The extent of the curve is its length, which is denoted as $\mathbb{L}_\alpha$. The boundary of the curve consists of the two end-points of the curve denoted $\Gamma_{\alpha 1}$ and $\Gamma_{\alpha 2}$ where $\Gamma_{\alpha m} \subset \mathbb{R}^0$ for $m \in \mathfrak{I}_{\Gamma_\alpha}$ and $\mathfrak{I}_{\Gamma_\alpha} = \{1, 2\}$. In contrast to the phase and interface boundaries, for which the boundary is continuous, the boundary of a common curve is formed by two disconnected points. The outward unit vectors that are tangent to Ω_α at the two end points are denoted $\mathbf{n}_\alpha$. The unit vector tangent to the curve is $\mathbf{l}_\alpha$. Therefore at one end of Ω_α, $\mathbf{n}_\alpha \cdot \mathbf{l}_\alpha = 1$ and at the other end, $\mathbf{n}_\alpha \cdot \mathbf{l}_\alpha = -1$. The velocity of the common curve is denoted as $\mathbf{w}_\alpha$. In directions normal to the common curve, the velocity of material in the common curve must be equal to the velocity of the common curve such that $(\mathbf{v}_\alpha - \mathbf{w}_\alpha) \cdot (\mathsf{I} - \mathbf{l}_\alpha \mathbf{l}_\alpha) = \mathbf{0}$. We

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[6] A common curve is also the location where three interfaces meet. If the indexes of the interfaces that exist between pairs of the three phases β, γ, and δ are denoted as $\beta\gamma$, $\beta\delta$, and $\gamma\delta$, the domain of the common curve can alternatively be defined as $\Omega_\alpha = \bar{\Omega}_{\beta\gamma} \cap \bar{\Omega}_{\beta\delta} \cap \bar{\Omega}_{\gamma\delta}$.

will denote the unit tensor for the curve as the 3×3 tensor $\mathbf{l}''_\alpha$ for the curve such that $\mathbf{l}''_\alpha = \mathbf{l}_\alpha \mathbf{l}_\alpha$.

A general conservation equation based on species i in common curve entity α can be developed with reference to Eq. (2.8). A notational change must be introduced to account for the fact that the integral over the boundary reduces to a sum over two end points for a common curve. Thus the general balance equation is

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Omega_\alpha} F_{i\alpha}\, \mathrm{d}\mathfrak{r} + \sum_{m \in \mathfrak{I}_{\Gamma\alpha}} F_{i\alpha} \left(\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha\right) \cdot \mathbf{n}_\alpha |_{\Gamma_{\alpha m}} - \int\limits_{\Omega_\alpha} S_{\Omega T i\alpha}\, \mathrm{d}\mathfrak{r}$$

$$- \sum_{m \in \mathfrak{I}_{\Gamma\alpha}} \mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{n}_\alpha |_{\Gamma_{\alpha m}} - \int\limits_{\Omega_\alpha} G_{\Omega i\alpha}\, \mathrm{d}\mathfrak{r} = 0, \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{C} \,. \tag{2.89}$$

In this equation, all densities are per unit length, the domain of integration is a one-dimensional curve, and the summations are over the two end points that form the boundary of the curve. In the case when the common curve is closed, the summation terms do not appear. However, reduction of this equation for an entire curve to the part appropriate for a microscale segment inherently changes the equation to apply to a microscale segment that is not closed.

The conversion of this conservation equation for a common curve to the form that applies at a point along a curve requires that the boundary summation terms be converted to integrals over the common curve. Part of this task can be accomplished making use of the transport theorem [8]:

Theorem 2.5 (T[1,(0,0),1]) *For a smooth continuous and differentiable function f defined over a domain $\Omega_\alpha \subset I\!R^1$ that may deform with time t due to velocity $\mathbf{w}_\alpha$ of the domain and with boundary end points $\Gamma_{\alpha m}$ where $m \in \mathfrak{I}_{\Gamma\alpha}$, designate the unit tangent to the domain as $\mathbf{l}_\alpha$, the outward vector tangent to the domain at the end point boundaries as $\mathbf{n}_\alpha$, and the unit tensor $\mathbf{l}''_\alpha = \mathbf{l}_\alpha \mathbf{l}_\alpha$. Then,*

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Omega_\alpha(t)} f\, \mathrm{d}\mathfrak{r} = \int\limits_{\Omega_\alpha(t)} \frac{\partial'' f}{\partial t}\, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha(t)} f \mathbf{w}_\alpha \cdot \left(\nabla'' \cdot \mathbf{l}''_\alpha\right) \mathrm{d}\mathfrak{r} + \sum_{m \in \mathfrak{I}_{\Gamma\alpha}} f \mathbf{w}_\alpha \cdot \mathbf{n}_\alpha |_{\Gamma_{\alpha m}(t)} \,, \tag{2.90}$$

where the partial derivative with respect to time for a point fixed to Ω_α is defined as

$$\frac{\partial''}{\partial t} = \frac{\mathrm{d}}{\mathrm{d}t} - \mathbf{w}_\alpha \cdot \nabla'' \,; \tag{2.91}$$

and $\nabla'' \cdot$ and ∇'' are the curve divergence and curve gradient operators, respectively, defined as

$$\nabla'' \cdot = (\mathbf{l}''_\alpha \cdot \nabla) \cdot \tag{2.92}$$

and

$$\nabla'' = \mathbf{l}''_\alpha \cdot \nabla \,. \tag{2.93}$$

When in diagonal form, the tensor, $\mathbf{I}''_{\alpha}$ has an entry of 1 on the diagonal element aligned with the curve tangent and zeroes elsewhere. When f is the density of a conserved quantity with units of the property per unit length, the left side of Eq. (2.90) is the change in the total amount of the conserved quantity with time over the curve. This is equated to the three terms on the right that account, respectively, for the changes in the quantity per time due to changes in the density of the property at points on the curve, changes in the quantity due to movement of the curve that causes its curvature to change (i.e., the curve can change its length without movement of its end points), and movement of the end points of the curve that cause it to increase or decrease in length.

Also of use in transforming the general conservation equation is the curve divergence theorem [8]:

Theorem 2.6 (D[1,(0,0),1]) *For a smooth continuous and differentiable tensor function* $\mathbf{f}$ *defined over a domain* $\Omega_{\alpha} \subset I\!R^1$ *that may deform with time* t *due to velocity* $\mathbf{w}_{\alpha}$ *of the domain and with boundary end points* $\Gamma_{\alpha m}$ *where* $m \in \mathfrak{J}_{\Gamma_{\alpha}}$*, designate the unit vector tangent to the domain as* $\mathbf{l}_{\alpha}$*, the outward vector tangent to the domain at the end boundaries as* $\mathbf{n}_{\alpha}$*, and the unit tensor* $\mathbf{I}''_{\alpha} = \mathbf{l}_{\alpha}\mathbf{l}_{\alpha}$*. Then,*

$$\int\limits_{\Omega_{\alpha}(t)} \mathrm{div}''\mathbf{f}\,\mathrm{d}\mathfrak{r} = -\int\limits_{\Omega_{\alpha}(t)} \mathbf{f}\cdot\left(\nabla''\cdot\mathbf{I}''_{\alpha}\right)\mathrm{d}\mathfrak{r} + \sum_{m\in\mathfrak{J}_{\Gamma\alpha}} \mathbf{f}\cdot\mathbf{n}_{\alpha}\big|_{\Gamma_{\alpha m}(t)}\ , \tag{2.94}$$

where $\nabla''\cdot$ *is the curve divergence operator defined as*

$$\nabla''\cdot = \left(\mathbf{I}''_{\alpha}\cdot\nabla\right)\cdot\ ; \tag{2.95}$$

and div'' *is the divergence operator along the curve that contracts the last index of* $\mathbf{f}$*.*

It is left as an exercise to show that

$$\mathrm{div}''\mathbf{f} + \mathbf{f}\cdot\left(\nabla''\cdot\mathbf{I}''_{\alpha}\right) = \mathrm{div}''\left(\mathbf{f}\cdot\mathbf{I}''_{\alpha}\right)\ . \tag{2.96}$$

Making use of this relation, we can write an alternative, but equivalent, form of Eq. (2.94) as

$$\int\limits_{\Omega_{\alpha}(t)} \mathrm{div}''\left(\mathbf{f}\cdot\mathbf{I}''_{\alpha}\right)\mathrm{d}\mathfrak{r} = \sum_{\mathrm{m}\in\mathfrak{J}_{\Gamma\alpha}} \mathbf{f}\cdot\mathbf{n}_{\alpha}\big|_{\Gamma_{\alpha\mathrm{m}}(\mathrm{t})}\ . \tag{2.97}$$

With f replaced by $F_{i\alpha}$ in transport theorem Eq. (2.90), with $\mathbf{f}$ replaced by $F_{i\alpha}\mathbf{v}_{i\alpha}$ in divergence theorem Eq. (2.94), and $\mathbf{f}$ replaced by $\mathbf{S}_{\Gamma i\alpha}$ in alternative divergence theorem Eq. (2.97), equations are obtained that allow the boundary terms in Eq. (2.89) to be eliminated. The result is

$$\int\limits_{\Omega_{\alpha}} \left[\frac{\partial'' F_{i\alpha}}{\partial t} + \nabla''\cdot\left(\mathbf{v}_{i\alpha}F_{i\alpha}\right) + F_{i\alpha}\left(\mathbf{v}_{i\alpha} - \mathbf{w}_{\alpha}\right)\cdot\left(\nabla''\cdot\mathbf{I}''_{\alpha}\right)\right]\mathrm{d}\mathfrak{r}$$

$$-\int\limits_{\Omega_\alpha}\left[S_{\Omega Ti\alpha}+\mathrm{div}''\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathbf{l}''_\alpha\right)+\mathrm{G}_{\Omega i\alpha}\right]\mathrm{d}\mathfrak{r}=0\quad\text{for } i\in\mathfrak{I}_s,\alpha\in\mathfrak{I}_\mathrm{C}\,. \tag{2.98}$$

In this equation, $\nabla''\cdot\mathbf{l}''_\alpha$ is a vector accounting for the curvature of the domain and is normal to the curve. The vector product of this term with $\mathbf{v}_{i\alpha}-\mathbf{w}_\alpha$ is zero because mass in the curve moving in a direction normal to the curve moves at the velocity of the curve. The total body source for the curve is composed of three components. External sources acting on the entity are the first component. The common curve is located where three interfaces meet. These interfaces interact with the common curve and can exchange properties with the curve. Thus, at every point on the curve, the exchanges with the interfaces can be considered a second element of a body source. The third component arises from interaction of the common curve with a phase at locations where the surface has a unique normal. At these locations, interactions between the common curve and the phase is modeled as a concentrated force. This singularity, in general, can be composed of advective and non-advective components. Its mathematical form is the same as an interaction term from an interface to a common curve. In subsequent analysis of particular cases, although it is possible that an advective flow could occur directly from a common curve to a phase, this will not be considered. The non-advective component will be incorporated as it impacts common curve dynamics.[7] The concentrated interaction term will thus be a non-advective flux, such as stress or heat conduction. With these considerations in mind, we express the body source explicitly in terms of these three components as

$$S_{\Omega Ti\alpha}=S_{\Omega i\alpha}+\sum_{\kappa\in\mathfrak{I}^+_{\mathrm{c}\alpha}}\sum_{j\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{X}+\frac{1}{2}\sum_{\beta\in\mathfrak{I}^+_{\mathrm{c}\alpha}}\sum_{\kappa\in\mathfrak{I}^+_{\mathrm{c}\beta}}\sum_{j\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{X^*}\,, \tag{2.99}$$

where $\mathfrak{I}^+_{\mathrm{c}\alpha}$ is the connected set for common curve α that is of higher dimensionality (i.e., interfaces in the connected set), $\mathfrak{I}^+_{\mathrm{c}\beta}$ is the higher order connected set to these interfaces (i.e., phases), and $\underset{j\kappa\to i\alpha}{X}$ and $\underset{j\kappa\to i\alpha}{X^*}$ are the body source components due to transfer of the property being conserved from species j in entity κ to species i in entity α. For emphasis, a superscript $*$ is used to indicate a transfer term between a phase and a common curve is only non-zero if a concentrated force is operative where the normal direction to the solid is unique. The factor of 1/2 appears with the last term because the double sum over entities will encounter each phase twice.

Because the domain of integration is arbitrary, the integrand itself—not just the integral—must be zero. With the considerations of the last paragraph, the general microscale conservation or balance equation at a point on a common curve is then obtained from Eq. (2.98) as

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[7] This interaction can be conceptualized crudely as transport from a phase to a common curve through zero area. For such a transfer to occur, the quantity being transported would have some magnitude highly concentrated at the curve. The non-advective concentrated component of stress can be thought of as a normal force exerted by the solid that balances the forces of interfaces at the surface.

$$\frac{\partial'' F_{i\alpha}}{\partial t} + \nabla''\cdot(\mathbf{v}_{i\alpha}F_{i\alpha}) - S_{\Omega i\alpha} - \sum_{\kappa\in\mathfrak{J}^+_{\mathrm{c}\alpha}} \sum_{j\in\mathfrak{J}_s} \underset{j\kappa\to i\alpha}{X} - \frac{1}{2}\sum_{\beta\in\mathfrak{J}^+_{\mathrm{c}\alpha}} \sum_{\kappa\in\mathfrak{J}^+_{\mathrm{c}\beta}} \sum_{j\in\mathfrak{J}_s} \underset{j\kappa\to i\alpha}{X^*}$$
$$- \operatorname{div}''\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathbf{l}''_{\alpha}\right) - \mathrm{G}_{\Omega i\alpha} = 0 \quad \text{for } i\in\mathfrak{J}_{\mathrm{s}}, \alpha\in\mathfrak{J}_{\mathrm{C}}\,. \tag{2.100}$$

This equation may also be written in terms of the material derivative as

$$\frac{\mathrm{D}_{i\alpha} F_{i\alpha}}{\mathrm{D}t} + F_{i\alpha}\mathbf{l}''_{\alpha}{:}\mathbf{d}''_{i\alpha} - S_{\Omega i\alpha} - \sum_{\kappa\in\mathfrak{J}^+_{\mathrm{c}\alpha}} \sum_{j\in\mathfrak{J}_s} \underset{j\kappa\to i\alpha}{X} - \frac{1}{2}\sum_{\beta\in\mathfrak{J}^+_{\mathrm{c}\alpha}} \sum_{\kappa\in\mathfrak{J}^+_{\mathrm{c}\beta}} \sum_{j\in\mathfrak{J}_s} \underset{j\kappa\to i\alpha}{X^*}$$
$$- \operatorname{div}''\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathbf{l}''_{\alpha}\right) - \mathrm{G}_{\Omega i\alpha} = 0 \quad \text{for } i\in\mathfrak{J}_{\mathrm{s}}, \alpha\in\mathfrak{J}_{\mathrm{C}}\,, \tag{2.101}$$

where

$$\frac{\mathrm{D}_{i\alpha}}{\mathrm{D}t} = \frac{\partial''}{\partial t} + \mathbf{v}_{i\alpha}\cdot\nabla'' \tag{2.102}$$

and

$$\mathbf{d}''_{i\alpha} = \left[\nabla''\mathbf{v}_{i\alpha} + \left(\nabla''\mathbf{v}_{i\alpha}\right)^{\mathrm{T}}\right]\,. \tag{2.103}$$

Although Eqs. (2.100) and (2.101) are equivalent forms, the former is more convenient to work with for averaging to obtain larger scale equations.

2.5.2 Specific Conservation and Balance Principles

A comparison of the general point equation for a common curve, Eq. (2.100), with the corresponding equation for a surface, Eq. (2.67), indicates that the equations appear to be different only in the domain, the number of primes in the differential operator and the unit tensor, and in the exchanges with entities two-dimensions higher. When a single prime is used, the differentiation occurs on a surface, while a double prime indicates differentiation on a curve. Both definitions of the material derivatives given by Eqs. (2.69) and (2.102) are time derivatives following the movement of a particle and are equivalent. An important difference between the surface and curve equations is related to the definition of the source terms, $\mathbf{S}_{\Gamma\alpha}$. Based on the similarities, Tables 2.3 and 2.4 can be used to motivate the specific forms of equations for common curves with allowances made for the particular features of the common curve equations. The corresponding results for species and entity equations are collected in Tables 2.5 and 2.6, respectively. In these tables, the domain of α has been changed from $\mathfrak{J}_{\mathrm{I}}$ to $\mathfrak{J}_{\mathrm{C}}$ and the single prime $(')$ is replaced by a double prime $('')$ in all instances. The connected set, $\mathfrak{J}^+_{\mathrm{c}\alpha}$, refers to the three interfaces that meet to form the common curve. The specific balance equations for a common curve are obtained with minor cosmetic differences in notation and will be listed here in their partial time derivative forms. The forms in terms of material derivatives also follow directly.

The most noticeable change between the interface and common curve equation is the presence of the asterisk terms as body sources. These terms appear in the

Table 2.5 Physical variables for species-based common curve equations in partial derivative or material derivative form. $\mathcal{M}_{i\alpha}$, $\boldsymbol{\mathcal{P}}_{i\alpha}$, $\mathcal{E}_{i\alpha}$, $\mathcal{S}_{i\alpha}$, and $\mathcal{G}_{i\alpha}$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential for species i in common curve α. Terms with an asterisk describe exchanges between a common curve and a phase. Exchange terms are written in terms of microscale variables at the end of the table

$$\mathcal{F}_{i\alpha} = \frac{\partial'' F_{i\alpha}}{\partial t} + \nabla''\cdot\left(\mathbf{v}_{i\alpha}F_{i\alpha}\right) - S_{\Omega i\alpha} - \sum_{\kappa\in\mathfrak{I}^+_{c\alpha}}\sum_{j\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{X} - \frac{1}{2}\sum_{\beta\in\mathfrak{I}^+_{c\alpha}}\sum_{\kappa\in\mathfrak{I}^+_{c\beta}}\sum_{j\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{X^*}$$
$$-\mathrm{div}''\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathbf{l}''_\alpha\right) - G_{\Omega i\alpha} = 0 \quad \text{for } i\in\mathfrak{I}_s, \alpha\in\mathfrak{I}_C$$

$$\mathcal{F}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha}F_{i\alpha}}{\mathrm{D}t} + F_{i\alpha}\mathbf{l}''_\alpha:\mathbf{d}''_{i\alpha} - S_{\Omega i\alpha} - \sum_{\kappa\in\mathfrak{I}^+_{c\alpha}}\sum_{j\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{X} - \frac{1}{2}\sum_{\beta\in\mathfrak{I}^+_{c\alpha}}\sum_{\kappa\in\mathfrak{I}^+_{c\beta}}\sum_{j\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{X^*}$$
$$-\mathrm{div}''\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathbf{l}''_\alpha\right) - G_{\Omega i\alpha} = 0 \quad \text{for } i\in\mathfrak{I}_s, \alpha\in\mathfrak{I}_C$$

$\mathcal{F}_{i\alpha}$	$F_{i\alpha}$	$S_{\Omega i\alpha}$	$\underset{j\kappa\to i\alpha}{X}$	$\mathbf{S}_{\Gamma i\alpha}$	$G_{\Omega i\alpha}$
$\mathcal{M}_{i\alpha}$	$\rho_\alpha\omega_{i\alpha}$	—	$\delta_{ij}\underset{i\kappa\to i\alpha}{M}$	—	$r_{i\alpha}$
$\boldsymbol{\mathcal{P}}_{i\alpha}$	$\rho_\alpha\omega_{i\alpha}\mathbf{v}_{i\alpha}$	$\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}$	$\delta_{ij}\mathbf{v}_{i\kappa}\underset{i\kappa\to i\alpha}{M} + \underset{j\kappa\to i\alpha}{\mathbf{T}}$	$\mathbf{t}_{i\alpha}$	$\mathbf{p}_{i\alpha} + r_{i\alpha}\mathbf{v}_{i\alpha}$
$\mathcal{E}_{i\alpha}$	$E_{i\alpha}$ $+\rho_\alpha\omega_{i\alpha}\dfrac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}$	$\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha}$ $+h_{i\alpha}$	$\delta_{ij}\left(\dfrac{E_{i\kappa}}{\rho_\kappa\omega_{i\kappa}} + \dfrac{\mathbf{v}_{i\kappa}\cdot\mathbf{v}_{i\kappa}}{2}\right)\underset{i\kappa\to i\alpha}{M}$ $+\mathbf{v}_{j\kappa}\cdot\underset{j\kappa\to i\alpha}{\mathbf{T}} + \underset{j\kappa\to i\alpha}{Q}$	$\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\cdot\mathbf{v}_{i\alpha}$ $+\mathbf{q}_{i\alpha}$	$e_{i\alpha} + \mathbf{p}_{i\alpha}\cdot\mathbf{v}_{i\alpha}$ $+r_{i\alpha}\dfrac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}$
$\mathcal{S}_{i\alpha} - \Lambda_{i\alpha}$	$\eta_{i\alpha}$	$b_{i\alpha}$	$\delta_{ij}\dfrac{\eta_{i\kappa}}{\rho_\kappa\omega_{i\kappa}}\underset{i\kappa\to i\alpha}{M} + \underset{j\kappa\to i\alpha}{\Phi}$	$\boldsymbol{\varphi}_{i\alpha}$	$\Lambda_{i\alpha}$
$\mathcal{G}_{i\alpha}$	$\Psi_{i\alpha}$	$-\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha}$	$\delta_{ij}\underset{i\kappa\to i\alpha}{M}\psi_{i\alpha}$	—	$\rho_\alpha\omega_{i\alpha}\Big[\dfrac{\partial''\psi_{i\alpha}}{\partial t}$ $+\mathbf{g}_{i\alpha}\cdot\left(\mathbf{I} - \mathbf{l}''_\alpha\right)\cdot\mathbf{v}_{i\alpha}\Big]$ $+r_{i\alpha}\psi_{i\alpha}$

Inter-entity Exchange Terms

$\underset{i\kappa\to i\alpha}{M} = \mathbf{n}_\kappa\cdot\left[\rho_\kappa\omega_{i\kappa}\left(\mathbf{v}_{i\kappa} - \mathbf{v}_\alpha\right)\right]$ for $\kappa\in\mathfrak{I}^+_{c\alpha}$	$\underset{j\kappa\to i\alpha}{M^*} = 0$ for $\beta\in\mathfrak{I}^+_{c\alpha}, \kappa\in\mathfrak{I}^+_{c\beta}$
$\underset{j\kappa\to i\alpha}{\mathbf{T}} = -\underset{j\kappa\to i\alpha}{z_T}\mathbf{t}_{j\kappa}\cdot\mathbf{n}_\kappa$ for $\kappa\in\mathfrak{I}^+_{c\alpha}$;	$\underset{j\kappa\to i\alpha}{\mathbf{T}^*} = -\underset{j\kappa\to i\alpha}{z^*_T}\mathbf{t}^*_{j\kappa}\cdot\mathbf{n}_\kappa$ for $\beta\in\mathfrak{I}^+_{c\alpha}, \kappa\in\mathfrak{I}^+_{c\beta}$
$\underset{j\kappa\to i\alpha}{Q} = -\underset{j\kappa\to i\alpha}{z_Q}\mathbf{q}_{j\kappa}\cdot\mathbf{n}_\kappa$ for $\kappa\in\mathfrak{I}^+_{c\alpha}$;	$\underset{j\kappa\to i\alpha}{Q^*} = -\underset{j\kappa\to i\alpha}{z^*_Q}\mathbf{q}^*_{j\kappa}\cdot\mathbf{n}_\kappa$ for $\beta\in\mathfrak{I}^+_{c\alpha}, \kappa\in\mathfrak{I}^+_{c\beta}$
$\underset{j\kappa\to i\alpha}{\Phi} = -\underset{j\kappa\to i\alpha}{z_\Phi}\boldsymbol{\varphi}_{j\kappa}\cdot\mathbf{n}_\kappa$ for $\kappa\in\mathfrak{I}^+_{c\alpha}$	$\underset{j\kappa\to i\alpha}{\Phi^*} = -\underset{j\kappa\to i\alpha}{z^*_\Phi}\boldsymbol{\varphi}^*_{j\kappa}\cdot\mathbf{n}_\kappa$ for $\beta\in\mathfrak{I}^+_{c\alpha}, \kappa\in\mathfrak{I}^+_{c\beta}$

body force terms for the momentum, energy, and entropy equations. These terms account solely for exchanges between a phase and a common curve on the boundary of the phase when the normal to the phase is unique at the common curve. If the normal is non-unique, an exchange between the phase and the common curve is accomplished through the interfaces. The quantity exchanged to the common curve must come from a concentrated flux in the phase, which contributes to the common curve dynamics as a body source. This arises through modeling of the small surface region where the concentrated source exists as a common curve with no width. In Tables 2.5 and 2.6, it can be seen that, for the sake of generality, the summation occurs over the three phases that meet at the common curve. However, at most only one of the phases can have a smooth boundary at the common curve. Thus, for a phase κ, if $\mathbf{n}_\kappa$ is not unique at a common curve, the concentrated momentum, energy, and entropy fluxes of phase κ must all be zero at the common curve.

For the porous media problems we will be studying, only the solid phase will be allowed to have a unique boundary normal at the common curve. Thus the concentrated fluxes will be zero for fluid phases but may be non-zero for the solid. We have not considered advective fluxes from a phase to a common curve. The concentrated terms could be important, for example, in describing the forces acting in the normal direction to the solid exerted by interfaces that meet at a common curve. Alternatively, a common curve with very high heat conductivity on a smooth surface of a phase could exchange heat directly with the phase. The concentrated flux terms are defined at the bottom of Tables 2.5 and 2.6. The factor 1/2 appears in the definitions because, if one makes use of the prescribed summations, each phase is encountered twice. The counterparts to these terms that account for exchanges between the common curve and the interfaces that meet at the common curve retain the same definitions as provided at the bottom of Tables 2.3 and 2.4.

Based on the $\mathcal{M}_{i\alpha}$ row of Table 2.5, the point microscale conservation of mass equation for species i in common curve α is given by

$$\mathcal{M}_{i\alpha} = \frac{\partial''(\rho_\alpha \omega_{i\alpha})}{\partial t} + \nabla''\cdot(\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}) - \sum_{\kappa \in \mathfrak{I}^+_{c\alpha}} \underset{i\kappa\to i\alpha}{M} - r_{i\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_C\,. \tag{2.104}$$

From row $\mathcal{M}_\alpha$ of Table 2.6 or from summation of Eq. (2.104) over all species in Ω_α, the point microscale conservation of mass equation for a common curve α is

$$\mathcal{M}_\alpha = \frac{\partial''\rho_\alpha}{\partial t} + \nabla''\cdot(\rho_\alpha \mathbf{v}_\alpha) - \sum_{\kappa \in \mathfrak{I}^+_{c\alpha}} \underset{\kappa\to\alpha}{M} = 0 \quad \text{for } \alpha \in \mathfrak{I}_C\,. \tag{2.105}$$

The conservation of momentum equation for a species in a common curve based on Table 2.5 is written as

$$\begin{aligned}\mathcal{P}_{i\alpha} = {} & \frac{\partial''(\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha})}{\partial t} + \nabla''\cdot(\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \mathbf{v}_{i\alpha}) - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \\ & - \sum_{\kappa \in \mathfrak{I}^+_{c\alpha}} \sum_{j \in \mathfrak{I}_s} \left(\delta_{ij} \mathbf{v}_{i\kappa} \underset{i\kappa\to i\alpha}{M} + \underset{j\kappa\to i\alpha}{\mathbf{T}} \right) - \frac{1}{2} \sum_{\beta \in \mathfrak{I}^+_{c\alpha}} \sum_{\kappa \in \mathfrak{I}^+_{c\beta}} \sum_{j \in \mathfrak{I}_s} \underset{j\kappa\to i\alpha}{\mathbf{T}^*} \\ & - \nabla''\cdot\left(\mathbf{I}''_\alpha \cdot \mathbf{t}_{i\alpha}{}^{\mathrm{T}}\right) - \mathbf{p}_{i\alpha} - r_{i\alpha} \mathbf{v}_{i\alpha} = \mathbf{0} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_C\,. \end{aligned} \tag{2.106}$$

The entity-based conservation of momentum equation for a common curve that makes use of information in Table 2.6 is

$$\mathcal{P}_\alpha = \frac{\partial''(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \nabla''\cdot(\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha) - \rho_\alpha \mathbf{g}_\alpha - \sum_{\kappa \in \mathfrak{I}^+_{c\alpha}} \left(\mathbf{v}_\kappa \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\mathbf{T}} \right)$$

Table 2.6 Physical variables for entity-based common curve equations in partial derivative or material derivative form. $\mathcal{M}_\alpha$, $\boldsymbol{\mathcal{P}}_\alpha$, $\mathcal{E}_\alpha$, $\mathcal{S}_\alpha$, and $\mathcal{G}_\alpha$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential in common curve α. Terms with an asterisk describe possible exchanges between the common curve and a phase with a unique normal at the common curve. Exchange terms are at the end of the table

$$\mathcal{F}_\alpha = \frac{\partial'' F_\alpha}{\partial t} + \nabla''\cdot(\mathbf{v}_\alpha F_\alpha) - S_{\Omega\alpha} - \sum_{\kappa\in\mathcal{J}_{c\alpha}^+} \underset{\kappa\to\alpha}{X} - \frac{1}{2}\sum_{\beta\in\mathcal{J}_{c\alpha}^+}\sum_{\kappa\in\mathcal{J}_{c\beta}^+} \underset{\kappa\to\alpha}{X^*}$$
$$-\mathrm{div}''\left(\mathbf{S}_{\Gamma\alpha}\cdot\mathbf{l}''_\alpha\right) - G_{\Omega\alpha} = 0 \quad \text{for } \alpha\in\mathcal{J}_\mathrm{C}$$

$$\mathcal{F}_{*\alpha} = \frac{\mathrm{D}_\alpha F_\alpha}{\mathrm{D}t} + F_\alpha\mathbf{l}''_\alpha{:}\mathbf{d}''_\alpha - S_{\Omega\alpha} - \sum_{\kappa\in\mathcal{J}_{c\alpha}^+} \underset{\kappa\to\alpha}{X} - \frac{1}{2}\sum_{\beta\in\mathcal{J}_{c\alpha}^+}\sum_{\kappa\in\mathcal{J}_{c\beta}^+} \underset{\kappa\to\alpha}{X^*}$$
$$-\mathrm{div}''\left(\mathbf{S}_{\Gamma\alpha}\cdot\mathbf{l}''_\alpha\right) - G_{\Omega\alpha} = 0 \quad \text{for } \alpha\in\mathcal{J}_\mathrm{C}$$

$\mathcal{F}_\alpha$	F_α	$S_{\Omega\alpha}$	$\underset{\kappa\to\alpha}{X}$	$\underset{\kappa\to\alpha}{X^*}$	$\mathbf{S}_{\Gamma\alpha}$	$G_{\Omega\alpha}$
$\mathcal{M}_\alpha$	ρ_α	—	$\underset{\kappa\to\alpha}{M}$	—	—	—
$\boldsymbol{\mathcal{P}}_\alpha$	$\rho_\alpha\mathbf{v}_\alpha$	$\rho_\alpha\mathbf{g}_\alpha$	$\mathbf{v}_\kappa\underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\mathbf{T}}$	$\underset{\kappa\to\alpha}{\mathbf{T}^*}$	$\mathbf{t}_\alpha$	—
$\mathcal{E}_\alpha$	E_α $+\rho_\alpha\dfrac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}$ $+\rho_\alpha K_{E\alpha}$	$\rho_\alpha\mathbf{g}_\alpha\cdot\mathbf{v}_\alpha$ $+h_\alpha$ $+\sum_{i\in\mathcal{J}_s}\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{l}''_\alpha\cdot\mathbf{u}_{i\alpha}$	$\left(\dfrac{E_\kappa}{\rho_\kappa} + \dfrac{\mathbf{v}_\kappa\cdot\mathbf{v}_\kappa}{2}\right.$ $\left.+K_{E\kappa}\right)\underset{\kappa\to\alpha}{M}$ $+\mathbf{v}_\kappa\cdot\underset{\kappa\to\alpha}{\mathbf{T}} + \underset{\kappa\to\alpha}{Q}$	$\mathbf{v}_\kappa\cdot\underset{\kappa\to\alpha}{\mathbf{T}^*}$ $+\underset{\kappa\to\alpha}{Q^*}$	$\mathbf{t}_\alpha{}^\mathrm{T}\cdot\mathbf{v}_\alpha$ $+\mathbf{q}_\alpha$	—
$\mathcal{S}_\alpha - \Lambda_\alpha$	η_α	b_α	$\dfrac{\eta_\kappa}{\rho_\kappa}\underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\Phi}$	$\underset{\kappa\to\alpha}{\Phi^*}$	$\boldsymbol{\varphi}_\alpha$	Λ_α
$\mathcal{G}_\alpha$	Ψ_α	$-\rho_\alpha\mathbf{g}_\alpha\cdot\mathbf{v}_\alpha$ $-\sum_{i\in\mathcal{J}_s}\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{l}''_\alpha\cdot\mathbf{u}_{i\alpha}$	$\sum_{i\in\mathcal{J}_s}\underset{i\kappa\to i\alpha}{M}\psi_{i\alpha}$	—	$-\sum_{i\in\mathcal{J}_s}\rho_\alpha\omega_{i\alpha}\psi_{i\alpha}\mathbf{u}_{i\alpha}$	$\sum_{i\in\mathcal{J}_s}\rho_\alpha\omega_{i\alpha}\left[\dfrac{\partial''\psi_{i\alpha}}{\partial t}\right.$ $\left.+\mathbf{g}_{i\alpha}\cdot\left(\mathbf{I}-\mathbf{l}''_\alpha\right)\cdot\mathbf{v}_{i\alpha}\right]$ $+\sum_{i\in\mathcal{J}_s} r_{i\alpha}\psi_{i\alpha}$

Inter-entity Exchange Terms
$\underset{\kappa\to\alpha}{M} = \sum_{i\in\mathcal{J}_s}\underset{i\kappa\to i\alpha}{M} \quad \text{for } \kappa\in\mathcal{J}_{c\alpha}^+$
$\underset{\kappa\to\alpha}{\mathbf{T}} = \sum_{j\in\mathcal{J}_s}\sum_{i\in\mathcal{J}_s}\left[\underset{j\kappa\to i\alpha}{\mathbf{T}} + \delta_{ij}(\mathbf{v}_{i\kappa}-\mathbf{v}_\kappa)\underset{i\kappa\to i\alpha}{M}\right] \quad \text{for } \kappa\in\mathcal{J}_{c\alpha}^+$
$\underset{\kappa\to\alpha}{Q} = \sum_{j\in\mathcal{J}_s}\sum_{i\in\mathcal{J}_s}\left\{\underset{j\kappa\to i\alpha}{Q} + (\mathbf{v}_{j\kappa}-\mathbf{v}_\kappa)\cdot\underset{j\kappa\to i\alpha}{\mathbf{T}} + \delta_{ij}\left[\dfrac{E_{i\kappa}}{\rho_\kappa\omega_{i\kappa}} + \dfrac{\mathbf{u}_{i\kappa}\cdot\mathbf{u}_{i\kappa}}{2} - \left(\dfrac{E_\kappa}{\rho_\kappa} + K_{E\kappa}\right)\right]\underset{i\kappa\to i\alpha}{M}\right\} \quad \text{for } \kappa\in\mathcal{J}_{c\alpha}^+$
$\underset{\kappa\to\alpha}{\Phi} = \sum_{j\in\mathcal{J}_s}\sum_{i\in\mathcal{J}_s}\left\{\underset{j\kappa\to i\alpha}{\Phi} + \delta_{ij}\left[\dfrac{\eta_{i\kappa}}{\rho_\kappa\omega_{i\kappa}} - \dfrac{\eta_\kappa}{\rho_\kappa}\right]\underset{i\kappa\to i\alpha}{M}\right\} \quad \text{for } \kappa\in\mathcal{J}_{c\alpha}^+$
$\underset{\kappa\to\alpha}{\mathbf{T}^*} = -\mathbf{n}_\kappa\cdot\mathbf{t}^*_\kappa = \sum_{i\in\mathcal{J}_s}\sum_{j\in\mathcal{J}_s}\underset{j\kappa\to i\alpha}{\mathbf{T}^*} \quad \text{for } \beta\in\mathcal{J}_{c\alpha}^+, \kappa\in\mathcal{J}_{c\beta}^+$
$\underset{\kappa\to\alpha}{Q^*} = -\mathbf{n}_\kappa\cdot(\mathbf{t}^*_\kappa\cdot\mathbf{v}_\kappa + \mathbf{q}^*_\kappa) = \sum_{i\in\mathcal{J}_s}\sum_{j\in\mathcal{J}_s}\left[(\mathbf{v}_{j\kappa}-\mathbf{v}_\kappa)\cdot\underset{j\kappa\to i\alpha}{\mathbf{T}^*} + \underset{j\kappa\to i\alpha}{Q^*}\right] \quad \text{for } \beta\in\mathcal{J}_{c\alpha}^+, \kappa\in\mathcal{J}_{c\beta}^+$
$\underset{\kappa\to\alpha}{\Phi^*} = -\mathbf{n}_\kappa\cdot\varphi^*_\kappa = \sum_{i\in\mathcal{J}_s}\sum_{j\in\mathcal{J}_s}\underset{j\kappa\to i\alpha}{\Phi^*} \quad \text{for } \beta\in\mathcal{J}_{c\alpha}^+, \kappa\in\mathcal{J}_{c\beta}^+$

$$-\frac{1}{2}\sum_{\beta\in\mathcal{J}_{c\alpha}^+}\sum_{\kappa\in\mathcal{J}_{c\beta}^+}\underset{\kappa\to\alpha}{\mathbf{T}^*} - \nabla''\cdot\left(\mathbf{l}''_\alpha\cdot\mathbf{t}_\alpha\right) = \mathbf{0} \quad \text{for } \alpha\in\mathcal{J}_\mathrm{C}\,. \tag{2.107}$$

The species-based and entity-based conservation of energy equations for a common curve, extracted from Tables 2.5 and 2.6 are, respectively,

$$\begin{aligned}
\mathcal{E}_{i\alpha} = & \frac{\partial''}{\partial t}\left(E_{i\alpha}+\rho_\alpha\omega_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right)+\nabla''\cdot\left[\left(E_{i\alpha}+\rho_\alpha\omega_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right)\mathbf{v}_{i\alpha}\right] \\
& -\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha}-h_{i\alpha} \\
& -\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\sum_{j\in\mathfrak{I}_s}\left[\delta_{ij}\left(\frac{E_{i\kappa}}{\rho_\kappa\omega_{i\kappa}}+\frac{\mathbf{v}_{i\kappa}\cdot\mathbf{v}_{i\kappa}}{2}\right)\underset{i\kappa\to i\alpha}{M}+\mathbf{v}_{j\kappa}\cdot\underset{j\kappa\to i\alpha}{\mathbf{T}}+\underset{j\kappa\to i\alpha}{Q}\right] \\
& -\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{+}}\sum_{j\in\mathfrak{I}_s}\left(\mathbf{v}_{j\kappa}\cdot\underset{j\kappa\to i\alpha}{\mathbf{T}^{*}}+\underset{j\kappa\to i\alpha}{Q^{*}}\right) \\
& -\nabla''\cdot\left[\mathsf{l}''_\alpha\cdot\left(\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\cdot\mathbf{v}_{i\alpha}+\mathbf{q}_{i\alpha}\right)\right]-e_{i\alpha}-\mathbf{p}_{i\alpha}\cdot\mathbf{v}_{i\alpha}-r_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}=0 \\
& \qquad\qquad\qquad\qquad\qquad\qquad \text{for } i\in\mathfrak{I}_s, \alpha\in\mathfrak{I}_{\mathrm{C}}
\end{aligned} \tag{2.108}$$

and

$$\begin{aligned}
\mathcal{E}_{\alpha} = & \frac{\partial''}{\partial t}\left[E_\alpha+\rho_\alpha\left(\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}+K_{E\alpha}\right)\right]+\nabla''\cdot\left\{\left[E_\alpha+\rho_\alpha\left(\frac{\mathbf{v}_\alpha\cdot\mathbf{v}_\alpha}{2}+K_{E\alpha}\right)\right]\mathbf{v}_\alpha\right\} \\
& -\rho_\alpha\mathbf{g}_\alpha\cdot\mathbf{v}_\alpha-\sum_{i\in\mathfrak{I}_s}\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{u}_{i\alpha}-h_\alpha \\
& -\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\left[\left(\frac{E_\kappa}{\rho_\kappa}+\frac{\mathbf{v}_\kappa\cdot\mathbf{v}_\kappa}{2}\right)\underset{\kappa\to\alpha}{M}+\mathbf{v}_\kappa\cdot\underset{\kappa\to\alpha}{\mathbf{T}}+\underset{\kappa\to\alpha}{Q}\right] \\
& -\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{+}}\left(\mathbf{v}_\kappa\cdot\underset{\kappa\to\alpha}{\mathbf{T}^{*}}+\underset{\kappa\to\alpha}{Q^{*}}\right)-\nabla''\cdot\left[\mathsf{l}''_\alpha\cdot\left(\mathbf{t}_\alpha\cdot\mathbf{v}_\alpha+\mathbf{q}_\alpha\right)\right]=0 \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{C}}\,.
\end{aligned} \tag{2.109}$$

The balance of entropy equation for a species in a common curve-based on Table 2.5 is

$$\begin{aligned}
\mathcal{S}_{i\alpha} = & \frac{\partial''\eta_{i\alpha}}{\partial t}+\nabla''\cdot\left(\eta_{i\alpha}\mathbf{v}_{i\alpha}\right)-b_{i\alpha}-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\sum_{j\in\mathfrak{I}_s}\left(\delta_{ij}\frac{\eta_{i\kappa}}{\rho_\kappa\omega_{i\kappa}}\underset{i\kappa\to i\alpha}{M}+\underset{j\kappa\to i\alpha}{\Phi}\right) \\
& -\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{+}}\sum_{j\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{\Phi^{*}}-\nabla''\cdot\left(\mathsf{l}''_\alpha\cdot\boldsymbol{\varphi}_{i\alpha}\right)=\Lambda_{i\alpha} \\
& \qquad\qquad\qquad\qquad\qquad\qquad \text{for } i\in\mathfrak{I}_s, \alpha\in\mathfrak{I}_{\mathrm{C}}\,.
\end{aligned} \tag{2.110}$$

The entropy balance summed over all species is

$$\mathcal{S}_{\alpha} = \frac{\partial''\eta_\alpha}{\partial t}+\nabla''\cdot\left(\eta_\alpha\mathbf{v}_\alpha\right)-b_\alpha-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\left(\frac{\eta_\kappa}{\rho_\kappa}\underset{\kappa\to\alpha}{M}+\underset{\kappa\to\alpha}{\Phi}\right)$$

$$-\frac{1}{2}\sum_{\beta\in\mathfrak{I}^{+}_{c\alpha}}\sum_{\kappa\in\mathfrak{I}^{+}_{c\beta}}\underset{\kappa\to\alpha}{\Phi^{*}}-\nabla''\cdot\left(\mathbf{l}''_{\alpha}\cdot\boldsymbol{\varphi}_{\alpha}\right)=\Lambda_{\alpha}\quad\text{for }\alpha\in\mathfrak{I}_{\mathrm{C}}\,. \tag{2.111}$$

Finally, the expression for the derivative of the body force potential on a curve that appears in Table 2.5 may be inferred from Table 2.3 for an interface or derived in a manner similar to that used to obtain the entry in that table. The resulting equation is

$$\begin{aligned}\mathcal{G}_{*i\alpha}=\;&\frac{\mathrm{D}_{i\alpha}\Psi_{i\alpha}}{\mathrm{D}t}+\Psi_{i\alpha}\mathbf{l}''_{\alpha}{:}\mathbf{d}''_{i\alpha}+\rho_{\alpha}\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha}-\sum_{\kappa\in\mathfrak{I}^{+}_{c\alpha}}\underset{i\kappa\to i\alpha}{M}\psi_{i\alpha}\\&-\rho_{\alpha}\omega_{i\alpha}\frac{\partial''\psi_{i\alpha}}{\partial t}-\rho_{\alpha}\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\left(\mathbf{I}-\mathbf{l}''_{\alpha}\right)\cdot\mathbf{v}_{i\alpha}-r_{i\alpha}\psi_{i\alpha}=0\quad\text{for }i\in\mathfrak{I}_{s},\alpha\in\mathfrak{I}_{\mathrm{C}}\,.\end{aligned} \tag{2.112}$$

For the common curve entity, the expression for $\mathcal{G}_{*\alpha}$ is obtained as

$$\begin{aligned}\mathcal{G}_{*\alpha}=\;&\frac{\mathrm{D}_{\alpha}\Psi_{\alpha}}{\mathrm{D}t}+\Psi_{\alpha}\mathbf{l}''_{\alpha}{:}\mathbf{d}''_{\alpha}+\nabla''\cdot\left(\sum_{i\in\mathfrak{I}_{s}}\rho_{\alpha}\omega_{i\alpha}\psi_{i\alpha}\mathbf{l}''_{\alpha}\cdot\mathbf{u}_{i\alpha}\right)\\&+\rho_{\alpha}\mathbf{g}_{\alpha}\cdot\mathbf{v}_{\alpha}+\sum_{i\in\mathfrak{I}_{s}}\rho_{\alpha}\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{l}''_{\alpha}\cdot\mathbf{u}_{i\alpha}-\sum_{i\in\mathfrak{I}_{s}}\sum_{\kappa\in\mathfrak{I}^{+}_{c\alpha}}\underset{i\kappa\to i\alpha}{M}\psi_{i\alpha}\\&-\sum_{i\in\mathfrak{I}_{s}}\rho_{\alpha}\omega_{i\alpha}\frac{\partial''\psi_{i\alpha}}{\partial t}-\sum_{i\in\mathfrak{I}_{s}}\rho_{\alpha}\mathbf{g}_{\alpha}\cdot\left(\mathbf{I}-\mathbf{l}''_{\alpha}\right)\cdot\mathbf{v}_{\alpha}\\&-\sum_{i\in\mathfrak{I}_{s}}r_{i\alpha}\psi_{i\alpha}=0\quad\text{for }i\in\mathfrak{I}_{s},\alpha\in\mathfrak{I}_{\mathrm{C}}\,.\end{aligned} \tag{2.113}$$

Additionally, the expressions for $\mathcal{T}_{\mathcal{G}*i\alpha}$ and $\mathcal{T}_{\mathcal{G}*\alpha}$ for the common curve are the same in appearance as the corresponding expressions for phases and interfaces, Eqs. (2.45) and (2.48), respectively. When applied to a common curve, the densities that appear in these expressions are mass per common curve length.

2.6 General Multispecies Formulation for a Common Point

Common points are the fourth type of entity of interest in the development of conservation and balance equations. Common points are the regions in a multiphase system that exist where four phases meet, which is also the confluence of four common curves. Common points are zero-dimensional objects that do not occupy any volume, area, or length in a system. The measure of the extent of a common point entity is the number of these points in the system.

The notion of conservation and balance principles for common points parallels the notion of these principles for an interface and common curve, with some notable differences. Small regions exist in a system composed of four or more phases where material properties undergo sharp changes due to the coalescence of these phases. Such a region of transition is treated conceptually as a common point.

Common points also play a role as locations at the end of common curves where mass, momentum, energy, and entropy can be exchanged among common curves that meet. The density of common points thus affects property exchanges and is a quantity of interest. Conventional multiphase porous medium models do not explicitly consider common point properties or their evolution with time. Here, conservation and balance equations for common points will be formulated so that they will be available for use in explicitly analyzing their impact on system behavior. We note that these points typically are of higher order importance in comparison to interfaces and common curves. Although they are difficult to model, only exist in systems composed of four or more phases, and have limited impact, the formulation of a comprehensive model requires that they be included at the onset. If it is desired to exclude these entities from a model, then an explicit assumption or set of assumptions can be employed and then examined in hindsight.

2.6.1 General Microscale Point Form

The equations for conservation or balance of a common point property apply to a domain, Ω_α, where $\alpha \in \mathfrak{I}_{\mathrm{Pt}}$ and $\mathfrak{I}_{\mathrm{Pt}}$ is the index set of the various types of common points as determined by which phases meet at the point. Thus α is in the index set of common points for which $\Omega_\alpha \subset \mathbb{R}^0$ and whose extent is equal to the number of points in the system denoted $\mathbb{N}_\alpha$. Because common points are zero dimensional, they do not have boundaries. This makes them different from the other entity types. Rather common points are formed where four phases meet such that $\Omega_\alpha = \bar{\Omega}_\beta \cap \bar{\Omega}_\gamma \cap \bar{\Omega}_\delta \cap \bar{\Omega}_\varepsilon$ where β, γ, δ, and $\varepsilon \in \mathfrak{I}_{\mathrm{P}}$.[8]

The easiest way to obtain the form of the microscale point conservation equation is by inference based on the form of Eq. (2.13) for a phase, Eq. (2.67) for an interface, and Eq. (2.100) for a common curve. We note a progression of increase in the primes in the equation as the dimensionality decreases such that the general species-based microscale equation for a common point is inferred to be

$$\frac{\partial''' F_{i\alpha}}{\partial t} + \nabla''' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega T i\alpha} - \mathrm{div}''' \left(\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}'''_\alpha \right) - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{Pt}} . \tag{2.114}$$

In this equation, the partial time derivative with three primes is an evaluation while holding none of the three spatial coordinates fixed. In other words, it is a time derivative evaluated moving with the common point. Note that a common point moves at

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[8] A common point is also the confluence of four common curves. When the common curves exist at the locations where three phases come together and the indexes of the four phases are β, γ, δ and ε, the indexes of the common curves can be denoted as $\beta\gamma\delta$, $\beta\gamma\varepsilon$, $\beta\delta\varepsilon$, and $\gamma\delta\varepsilon$. The domain of the common point can alternatively be indicated as $\Omega_\alpha = \bar{\Omega}_{\beta\gamma\delta} \cap \bar{\Omega}_{\beta\gamma\varepsilon} \cap \bar{\Omega}_{\beta\delta\varepsilon} \cap \bar{\Omega}_{\gamma\delta\varepsilon}$.

the same velocity as the material in the point and all species in the point. Therefore

$$\frac{\partial'''}{\partial t} = \frac{\mathrm{d}}{\mathrm{d}t} = \frac{\mathrm{D}_{i\alpha}}{\mathrm{D}t} = \frac{\mathrm{D}_{\alpha}}{\mathrm{D}t} \,. \tag{2.115}$$

In addition, $\nabla'''\cdot$ and div''' indicate divergence operators with all coordinates held constant. Therefore, the terms involving these operators are zero. From a physical perspective, a property constrained to exist only at a point cannot vary in space. Therefore, Eq. (2.114) reduces to

$$\frac{\partial''' F_{i\alpha}}{\partial t} - S_{\Omega T i\alpha} - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{Pt}} \,. \tag{2.116}$$

Specific forms for this equation can be developed by inserting symbols from Table 2.3 or Table 2.4. However, the meanings of the symbols are such that the items chosen for $F_{i\alpha}$ have units of quantity per point while $S_{\Omega_{i\alpha}}$ and $G_{\Omega_{i\alpha}}$ have units of the quantity per point per time. When the common point has no properties, the surviving terms provide a jump condition for common curve properties at the point such that what leaves one curve must enter the other curves.

As an example, the microscale conservation equation for a chemical species at a common point is obtained, based on Eqs. (2.115) and (2.116) and Table 2.3 as

$$\mathcal{M}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha}\left(\rho_\alpha \omega_{i\alpha}\right)}{\mathrm{D}t} - \sum_{\kappa \in \mathfrak{I}^+_{\mathrm{c}\alpha}} \underset{i\kappa \to i\alpha}{M} - r_{i\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{Pt}} \,, \tag{2.117}$$

where $\rho_\alpha \omega_{i\alpha}$ is the mass of species i at common point α. In this equation, we have not allowed for concentrated direct mass exchange between the common point and phases or interfaces. The values that κ takes on are the index values of the four common curves that terminate at the common point. Thus the summation term is the net flux of species i from the common curves to the common point. This sum will be zero if the mass of i at the common point does not change with time and there is no net reaction or set of reactions $r_{i\alpha}$ that produce species i.

For the momentum equation, the form taken is slightly more complex if one includes the concentrated non-advective fluxes in the equation. A common point can interact with a phase directly if the point lies on the boundary of a phase at a location where the normal to the boundary is unique. Additionally, if the point lies at the edge of an interface where the normal to the edge of the interface that is also tangent to the interface is unique a term needs to be included that accounts for the interaction with the interface. The entity-based general form of the body source term is

$$S_{\Omega T\alpha} = S_{\Omega\alpha} + \sum_{\kappa \in \mathfrak{I}^+_{\mathrm{c}\alpha}} \underset{\kappa \to \alpha}{X} + \frac{1}{2} \sum_{\beta \in \mathfrak{I}^+_{\mathrm{c}\alpha}} \sum_{\kappa \in \mathfrak{I}^+_{\mathrm{c}\beta}} \underset{\kappa \to \alpha}{X^*} + \frac{1}{6} \sum_{\chi \in \mathfrak{I}^+_{\mathrm{c}\alpha}} \sum_{\beta \in \mathfrak{I}^+_{\mathrm{c}\chi}} \sum_{\kappa \in \mathfrak{I}^+_{\mathrm{c}\beta}} \underset{\kappa \to \alpha}{X^*} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{Pt}} \,, \tag{2.118}$$

where the single summation accounts for exchanges with the common curves, the double sum accounts for exchanges with interfaces, and the triple sum accounts for exchanges with phases. These latter two groups can be employed when the normal to the entity is unique at the common point. Thus, for example, the momentum equation for a common point entity is

$$\begin{aligned}\mathcal{P}_{*\alpha} = {} & \frac{\mathrm{D}_\alpha(\rho_\alpha \mathbf{v}_\alpha)}{\mathrm{D}t} - \rho_\alpha \mathbf{g}_\alpha - \sum_{\kappa\in\mathfrak{J}^+_{\mathrm{c}\alpha}} \left(\mathbf{v}_\kappa \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\mathbf{T}}\right) \\ & - \frac{1}{2} \sum_{\beta\in\mathfrak{J}^+_{\mathrm{c}\alpha}} \sum_{\kappa\in\mathfrak{J}^+_{\mathrm{c}\beta}} \underset{\kappa\to\alpha}{\mathbf{T}^*} - \frac{1}{6} \sum_{\chi\in\mathfrak{J}^+_{\mathrm{c}\alpha}} \sum_{\beta\in\mathfrak{J}^+_{\mathrm{c}\chi}} \sum_{\kappa\in\mathfrak{J}^+_{\mathrm{c}\beta}} \underset{\kappa\to\alpha}{\mathbf{T}^*} = \mathbf{0} \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{Pt}}\,. \end{aligned} \tag{2.119}$$

Listing of the remaining conservation equations of mass, momentum, and energy and of the entropy balance equation for species-based and entity-based quantities is straightforward based on Eqs. (2.116) and (2.119) along with the notation for quantities given in the tables for interfaces and common curves. Note that the meanings of the quantities is altered for the common point equations. The explicit conservation statements are not listed here simply because, except for the inclusion of the concentrated flux from a phase to the common point, the equations are redundant with previous equations and listings. Additionally, we will not be exploring systems with four or more phases such that common point dynamics will not enter our analyses.

2.7 Summary

A cornerstone of mechanistic modeling is the continuum equations for conservation of mass, momentum, and energy, along with the balance equation of entropy. TCAT builds upon microscale conservation and balance equations as a foundation for formulation of larger-scale models. The purpose of this chapter was to develop the general point-form microscale conservation equations for a phase, an interface, a common curve, and a common point. These general point-form conservation equations were expressed for a species in an entity and for an overall entity that includes all species in the entity.

The general conservation and balance equations account for the different dimensionality of the entities and for the fact that higher dimensional entities serve as body sources for lower dimensional entities. The general conservation or balance equation for a species property can be written as

$$\mathcal{F}_{i\alpha} = \frac{\partial^{(n)} F_{i\alpha}}{\partial t} + \nabla^{(n)}\cdot(\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega T i\alpha} - \mathrm{div}^{(n)}\left(\mathbf{S}_{\Gamma\alpha}\cdot\mathbf{l}^{(n)}_{\alpha}\right) - G_{\Omega i\alpha} = 0$$
$$\text{for } i\in\mathfrak{J}_s, \alpha\in\mathfrak{J}, n = 3 - \dim\alpha, \tag{2.120}$$

or

$$\mathcal{F}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha} F_{i\alpha}}{\mathrm{D}t} + F_{i\alpha}\mathbf{I}_{\alpha}^{(n)}{:}\mathbf{d}^{(n)} - S_{\Omega T i\alpha} - \mathrm{div}^{(n)}\left(\mathbf{S}_{\Gamma i\alpha}\cdot\mathbf{I}_{\alpha}^{(n)}\right) - G_{\Omega i\alpha} = 0$$
$$\text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}, n = 3 - \dim\,\alpha\,, \qquad (2.121)$$

where dim α is the integer dimensionality of entity α such that $0 \leq \dim\,\alpha \leq 3$, (n) indicates the number of primes that appear in the equation with the primed time derivative, divergence operator, and strain tensor previously defined. We have adopted the convention of using the leftmost quantity to indicate an equation type (e.g., $\mathcal{F} = \mathcal{M}$ for mass conservation), and a specific form in terms of a partial derivative is indicated when there is no "$*$" in the subscript while a particular material derivative form corresponds to a designation with the "$*$" in the subscript. The body source $S_{\Omega T i\alpha}$ includes contributions from the next higher dimensional entity when dim α = 0, 1, or 2, from an entity two dimensions higher when dim $\alpha = 0$ or 1, and from a phase entity to a common point when dim $\alpha = 0$. The conservation or balance equation for an entity-based quantity is identical to Eq. (2.120) and Eq. (2.121) with the subscript i deleted. This is obtained by summing Eq. (2.120) over all species in the entity, and then rearranging if the material derivative form is desired. One needs to recognize, however, that although the sum of the species-based conservation equation in an entity provides the entity-based equation, the sum of an individual species-based variable does not always equal the corresponding variable for the entity.

Specific conservation and balance equations for each entity are formulated by mapping the physical variables for a given conservation or balance statement to the placeholder variables in the general equations. This approach allows for the simple identification of all microscale conservation and balance equations that will be built upon in this work. Exercises at the end of this chapter provide opportunities to master the concepts important to the derivations here.

Lastly, derivation of the conservation of angular momentum equations has not been included here because the role of this equation is primarily to demonstrate whether or not a stress tensor is symmetric. In this book, which is only an introduction to the TCAT approach, we will consider the stress tensor for an entity to be symmetric but allow the stress tensor for a species in an entity to be non-symmetric [1, 2, 14].

Exercises

2.1. Show that Eq. (2.37) may be written in the equivalent form:

$$\mathbf{q}_{\alpha} = \sum_{i\in\mathfrak{I}_s} \left[\mathbf{q}_{i\alpha} + \left(\mathbf{t}_{i\alpha}{}^{\mathrm{T}} - \omega_{i\alpha}\mathbf{t}_{\alpha}{}^{\mathrm{T}}\right)\cdot(\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha})\right]$$
$$- \sum_{i\in\mathfrak{I}_s} \left[(E_{i\alpha} - \omega_{i\alpha}E_{\alpha}) + \rho_{\alpha}\omega_{i\alpha}\frac{(\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha})\cdot(\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha})}{2}\right](\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha})\ . \qquad (2.122)$$

This form, though a bit lengthier, shows that the difference between $\mathbf{q}_\alpha$ and the sum over all species of $\mathbf{q}_{i\alpha}$ is a set of terms that are all products of deviations.

2.2. Show that Eq. (2.33) may equivalently be written

$$\sum_{i\in\mathfrak{J}_s}\left(e_{i\alpha}+\mathbf{p}_{i\alpha}\cdot\mathbf{u}_{i\alpha}+r_{i\alpha}\frac{\mathbf{u}_{i\alpha}\cdot\mathbf{u}_{i\alpha}}{2}\right)=0\,.$$

2.3. Show that the following definitions of a material derivative are equivalent:

$$\frac{\mathrm{D}_\alpha}{\mathrm{D}t}=\frac{\partial}{\partial t}+\mathbf{v}_\alpha\cdot\nabla=\frac{\partial'}{\partial t}+\mathbf{v}_\alpha\cdot\nabla'=\frac{\partial''}{\partial t}+\mathbf{v}_\alpha\cdot\nabla''\,. \tag{2.123}$$

2.4. Show that in the summation of Eq. (2.73) over $i\in\mathfrak{J}_s$ to obtain Eq. (2.74), one obtains

$$\begin{aligned}&\sum_{i\in\mathfrak{J}_s}\sum_{j\in\mathfrak{J}_s}\mathbf{n}_\kappa\cdot\left[\delta_{ij}\rho_\kappa\omega_{i\kappa}\mathbf{v}_{i\kappa}\left(\mathbf{v}_{i\kappa}-\mathbf{v}_\alpha\right)-\underset{j\kappa\to i\alpha}{z_T}\mathbf{t}_{j\kappa}{}^{\mathrm{T}}\right]\\&\qquad=\mathbf{n}_\kappa\cdot\left[\rho_\kappa\mathbf{v}_\kappa\left(\mathbf{v}_\kappa-\mathbf{v}_\alpha\right)-\mathbf{t}_\kappa\right]\quad\text{for }\alpha\in\mathfrak{J},\kappa\in\mathfrak{J}^+_{c\alpha}\,,\end{aligned} \tag{2.124}$$

where $\mathbf{t}_\kappa$ is defined as in Eq. (2.30) and $\mathbf{v}_\kappa$ is the barycentric velocity.

2.5. Show the following:

a. Equation (2.79) can be obtained as the sum of Eq. (2.78) over all species i in interface entity α.
b. The definitions of $\mathbf{t}_\alpha$ where $\alpha\in\mathfrak{J}_\mathrm{I}$ and $\mathbf{t}_\kappa$ where $\kappa\in\mathfrak{J}_{c\alpha}$ used in Eq. (2.79) satisfy Eq. (2.30).
c. The definitions of $\mathbf{q}_\alpha$ where $\alpha\in\mathfrak{J}_\mathrm{I}$ and $\mathbf{q}_\kappa$ where $\kappa\in\mathfrak{J}_{c\alpha}$ used in Eq. (2.79) satisfy Eq. (2.37).

2.6. Equation (2.30) defines the surface stress tensor in terms of species stress tensor. Show that for a surface, this equation also satisfies

$$\mathbf{t}_\alpha\cdot\mathbf{l}'_\alpha=\sum_{i\in\mathfrak{J}_s}\left[\mathbf{t}_{i\alpha}\cdot\mathbf{l}'_\alpha-\rho_\alpha\omega_{i\alpha}\mathbf{l}'_\alpha\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}_\alpha\right)\left(\mathbf{v}_{i\alpha}-\mathbf{v}_\alpha\right)\cdot\mathbf{l}'_\alpha\right]\quad\text{for }\alpha\in\mathfrak{J}_\mathrm{I}\,.$$

2.7. Prove Eq. (2.96) which states

$$\mathrm{div}''\mathbf{f}+\mathbf{f}\cdot\left(\nabla''\cdot\mathbf{l}''_\alpha\right)=\mathrm{div}''\left(\mathbf{f}\cdot\mathbf{l}''_\alpha\right)\quad\text{for }\alpha\in\mathfrak{J}_\mathrm{C}\,.$$

2.8. Show that for an α entity composed of two chemical species, designated as A and B, the general form of $K_{E\alpha}$ given in Eq. (2.35) may be simplified to

$$K_{E\alpha} = \omega_{A\alpha}\omega_{B\alpha}\frac{(\mathbf{v}_{A\alpha} - \mathbf{v}_{B\alpha})\cdot(\mathbf{v}_{A\alpha} - \mathbf{v}_{B\alpha})}{2} \ .$$

2.9. Write the explicit form of the momentum equation for a massless common point and provide a physical explanation for the terms in this equation.

2.10. The body force potential for a species, $\psi_{i\alpha}$, and the body force per mass of the species, $\mathbf{g}_{i\alpha}$, are related for all entities as given by Eq. (2.50) for a phase such that

$$\nabla\psi_{i\alpha} + \mathbf{g}_{i\alpha} = 0 \quad \text{for } i \in \mathfrak{I} \ .$$

a. Show that for a phase the entity-based identity is

$$\nabla\psi_{\alpha} + \mathbf{g}_{\alpha} = \sum_{i\in\mathfrak{I}_s} \nabla\omega_{i\alpha}\left(\psi_{i\alpha} - \psi_{N\alpha}\right) \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}} \ ,$$

where $N \in \mathfrak{I}_s$ is a reference species and ψ_α is defined for any entity as in Eq. (2.46).

b. Obtain the corresponding relation between $\nabla'\psi_\alpha$ and $\mathbf{g}_\alpha$ when $\alpha \in \mathfrak{I}_{\mathrm{I}}$.

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Chapter 3
Microscale Thermodynamics

3.1 Overview

Models of a system that are mechanistically based make use of the full range of physical principles that influence system behavior. Paramount among these are the conservation and balance equations as derived in Chap. 2. In addition to these expressions, the thermodynamic properties of the entities in the system, as well as of the system as a whole, impact the observed behavior. The thermodynamic relations that are hypothesized to describe a system impact how that system is modeled and the fidelity of the model compared to the actual behavior of the system. Thermodynamics plays a role not only in describing system properties and parameters but also in identifying limits on system behavior that might be observed. For example, thermodynamic considerations have led to equations of state for materials, definitions of compressibility, and definitions of heat capacity. Thermodynamics also rules out perpetual motion machines, identifies the interconversion of heat and work, and specifies the direction of heat exchange when a hot and a cold body come into contact. These features of system dynamics are outside the scope of constraints provided by conservation and balance equations.

Thermodynamic considerations play a key role in the formulation of closure relations for the conservation and balance equations so that the number of unknowns in the developed model equations matches the number of equations. Although thermodynamic relations may be employed at any length scale to obtain closure of conservation and balance equations at that scale, the TCAT method ensures that these relations are consistent across scales. Thus, a thermodynamic formalism will be hypothesized at the microscale, and the relations obtained will be transformed to a larger scale by a systematic mathematical procedure.

The purpose of this chapter is to introduce some basic concepts from thermodynamics that are relied upon throughout the remainder of the book. Thermodynamics has a rich, subtle, and complex history; the exposition provided here does no justice to this discipline. The focus is on a few of the basic principles such that we can proceed with the development of TCAT models. This focus is somewhat at odds

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with the development of the field of thermodynamics itself, which originated and has evolved as a field of study that is inextricably linked to and motivated by applications of profound interest in science and engineering. Nevertheless, the principles that result here find application in every complete and closed model to be formulated in subsequent chapters.

Classical thermodynamics deals with systems at equilibrium. All classical systems in which change is occurring tend to evolve to states that can be defined solely by intrinsic properties rather than by initial conditions or any knowledge of a path of change that may have been followed. When such a system becomes independent of applied external boundary conditions, the system is said to be in an equilibrium state. Equilibrium states are therefore static and independent of time. It is these equilibrium states that are described by classical thermodynamic relations.[1] Equilibrium thermodynamics (ET) can be subdivided further into the early thermodynamics of Clausius and Kelvin and more modern Gibbsian thermodynamics. [15, 51]. The former was developed by deriving important energy and work concepts based on the observations of the behavior of a system in response to various changes in variables or system construction. The observations led to the establishment of the internal energy and entropy functions. With the Gibbsian approach, the concepts of internal energy and entropy are assumed to be known. Coupling these quantities with a set of postulates about system behavior leads to useful mathematical relations among the variables. These two approaches to thermodynamics are consistent with each other but provide alternative perspectives. The motivation behind the development of Gibbsian thermodynamics was to obtain a framework within which the equilibrium properties of thermodynamics systems could be characterized [33]. The development here will proceed from the Gibbsian perspective making use of the postulational approach to equilibrium thermodynamics [1, 8, 25, 32, 47].

Because we are interested in the evolution of dynamic systems as described by conservation and balance equations, there is a need to extend thermodynamics beyond its classical roots so that it can contribute to dynamic descriptions of non-equilibrium systems. Several theoretical approaches to this extension can be found including classical irreversible thermodynamics (CIT), rational thermodynamics (RT), extended irreversible thermodynamics (EIT), rational extended thermodynamics (RET), and the theory of internal variables (TIV). These approaches share the goal of being able to incorporate non-equilibrium processes into thermodynamic descriptions. Insightful reviews of the elements of the methods can be found in the literature ([e.g., 20, 26, 31, 35, 39]). In short, CIT is the simplest extension to classical thermodynamics. It presumes that although a system may be changing in time and space, at each instant and location a quasi-equilibrium state exists such that local expressions of dependences of energy on independent variables follow directly from equilibrium thermodynamics [11, 18, 24, 49]. CIT is discussed in Sect. 3.11

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[1] For descriptive clarity, it would be better if classical "thermodynamics" were actually called classical "thermostatics" because it does not describe the dynamic nature of a system; it only describes static states that precede and follow a dynamic event. Classical thermodynamics provides no information about the rate of transition between equilibrium states or of the states of the system when not at equilibrium.

following the description of equilibrium thermodynamics. The other methods are mentioned briefly in Sect. 3.12, primarily for breadth purposes as they are neither detailed nor relied upon for the models developed in this book.

In this chapter, our focus will be on Gibbsian equilibrium thermodynamics and its extension to classical irreversible thermodynamics for microscale systems. CIT provides the simplest non-equilibrium theory that supports the development of consistent multiscale, multiphase porous medium models. By using the CIT approach, we will be able to connect thermodynamic expressions effectively with conservation principles. This enables the formulation of models that are consistent with both conservation principles and equilibrium thermodynamics and also guides the formulation of valid closure conditions that apply away from equilibrium. Any of the other non-equilibrium approaches could be employed, but the relatively simple CIT form is adequate for the purposes of this book. We note that whatever non-equilibrium formulation is selected, the change in scale of equations to a larger scale for use with larger scale conservation and balance equations will have to be accomplished in a consistent fashion.

Porous medium systems are composed of fluids, solids, interfaces, common curves, and common points. The most frequently encountered application of equilibrium thermodynamics and CIT is to fluids. The procedures and equations are the same for both liquids and gases. A fluid flows such that it takes the shape of its container. Also, if a tangential force, or shear stress, is applied to the surface of a fluid, the fluid will deform to mitigate the force. If the force is withdrawn, the fluid will not return to its original shape. For natural porous medium systems, the most common fluids encountered are air and water, but petroleum and synthetic organics are also commonly encountered. Solids, on the other hand, do not assume the shape of a container. Here, we will limit our discussion to elastic solids, that is solids that return to their original shape if a shear stress is applied to cause deformation and is then relieved. This precludes consideration of solids that are inelastic or are permanently deformed or fractured by application of a very high degree of stress. Note that in specifying this type of deformation, we are referring, for example, to the individual grains that make up the solid phase of a porous medium system when modeling the microscale. Modeling of the matrix structure as elastic is also typical. For natural porous media, commonly encountered solids are rock, sand, silt, and clay.[2] Accounting for the different responses of fluids and solids to stresses requires that their thermodynamic formulations be based on different postulates. Additionally, the Gibbsian approach to the thermodynamics of interfaces and common curves will be presented because these entities are extremely important to the behavior of multiphase systems. Here, fluid-fluid interfaces and fluid-solid interfaces will be modeled based on the same thermodynamic postulates. Common points will be treated as singularities in the system that possess no thermodynamic properties.

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[2] Although one can easily define solids and fluids, there are some materials that defy easy classification or whose behavior changes from solid to fluid depending on the applied stress. Examples include Silly Putty®, asphalt, and toothpaste. In this text we will assume that identification of the materials of interest as fluids or solids is unambiguous.

This restriction can be relaxed if it is desired to incorporate more complex common points.

3.2 Essence of Equilibrium Thermodynamics

Despite an absence of a sophisticated understanding of molecular dynamics, the field of quantitative equilibrium thermodynamics developed in the nineteenth century. Statistical mechanics and the kinetic theory of gases, which today support the relations of equilibrium thermodynamics, did not evolve until the twentieth century. Statistical mechanics provides understanding of the atomic and molecular behavior that give rise to the observed larger scale properties of systems. However, these larger scale properties and the relations among them can also be developed based on postulates about equilibrium systems. We note that at the molecular scale, atoms and molecules are in motion and can be moving to new locations within a system. Equilibrium was defined in Sect. 3.1 as being a static state, one that is independent of time. Thus, at the molecular scale, because of the continual rearrangement of molecules, one might infer that equilibrium does not occur.[3] Despite the molecular rearrangements in a fluid, an equilibrium configuration can be achieved at a larger continuum scale where the properties of a fluid observed at that scale are independent of time and space. A solid also can achieve a configuration at the continuum scale such that its properties are constant and at equilibrium. We will develop our formalism for thermodynamics here without reference to the molecular state, recognizing that when considering objects at a larger scale, some important system dynamics become subscale processes that must nevertheless be accounted for. This discussion points to the important fact that a condition of equilibrium at a large scale does not necessarily imply equilibrium at a smaller scale.

Before proceeding, we caution that the naming conventions employed for scales of observation must be clearly defined. Although there is little ambiguity about what is meant by the molecular scale, the fact that different larger observational scales are important in different fields has led to different conventions for identifying scales. Most thermodynamics texts use "microscale" to refer to the molecular scale and use the term "macroscale" to refer to a continuum scale. For equilibrium thermodynamics where system properties are uniform, there is no need to designate or differentiate between a range of continuum scales. For purposes of the present book, we refer to the smallest continuum scale as the "microscale." At the microscale, phases are juxtaposed with identifiable interfaces separating them. Because variation of properties in space is of importance in the multiphase systems of interest here, we also make use of the term "macroscale" to indicate a larger scale where the distinct boundaries between phases are not distinguishable. At the macroscale, phases are viewed as overlapping continua with each occupying a fraction of space.

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[3] It is useful to note that freedom of molecular motion is much less in a solid than in a fluid. Additionally, a temperature of absolute zero is one where all molecular motion stops such that, for an isolated system, equilibrium would be achieved at the molecular scale.

The interfaces between phases are only known in an average sense, making use of area measures such as the amount of interfacial area per volume and, perhaps, the average orientation of those areas. From a macroscale perspective, it is still possible to consider spatial variations in the properties of a system. The macroscale can be considered as a larger scale that filters out high spatial frequency variability of a property. The length scale of a system as a whole, or in a direction that the system spans, is referred to as the "megascale." At the megascale, variability of a property is not accounted for; rather the system is characterized as a whole by an average value of that property. The three different scales are important for formulation of problems with spatial variability. For equilibrium systems with no spatial variability of properties, the distinction among length scales is unimportant.

The origin of thermodynamic studies lies in a desire to provide relations among the properties of matter at equilibrium [8]. The development of thermodynamic formulas from a classical nineteenth century perspective considers systems and seeks relations for changes in system variables such as temperature, volume, and energy in response to heat being added to the system, pressure change, chemical reactions, or other stresses [e.g., the approach found in 12, 19, 36, 50]. An alternative, and equally valid, approach is to base the development of thermodynamic relations on a set of postulates about system behavior. Then, from these postulates, the thermodynamic equations can be developed. This more mathematical approach, in fact, requires few, yet simple, postulates to develop a thermodynamic framework that is consistent with the more physically based approach. We will follow the postulational approach here because of its elegance and because it provides the most direct path to obtaining the relations we need to integrate into the TCAT approach to modeling. The postulational approach is clearly developed in [8] and has been referred to as Callen's postulational approach [25].

3.3 Fluid-phase Equilibrium Thermodynamics

In this section, we will make use of Callen's postulational approach to obtain the fundamental functional form, the differential form, the Euler form, and the Gibbs-Duhem equation for a fluid phase. These equations are the fundamental relations on which equations of state and differential relations among variables are built. The presentation here is brief, concentrating on the elements of equilibrium thermodynamics of fluid phases that are most important to the implementation of the TCAT approach.

3.3.1 Fundamental and Differential Forms

The first postulate will be posed here in the context of a single fluid phase composed of *N* chemical species. The discussion refers to what is traditionally called a "simple" system. Such a system is large, homogeneous, and isotropic. Surface effects at the boundary of the system can be neglected. Electrodynamic effects are not considered. Furthermore, at this point, gravitational forces, which would impact the homogeneity of the system, are also not included in the formulation. Gravitational effects will be accounted for subsequently when we consider smaller scale aspects of a system. Similarly, at a later time we will consider thermodynamic formulations for solids, surfaces, and common curves. For a fluid phase as a whole, equilibrium states are postulated to exist that are described completely by the phase's internal energy, $\mathbb{E}$, volume, $\mathbb{V}$, and by the mass of each of the N chemical species present, $\mathbb{M}_i$, where the subscript i refers to each of the species. If the species present are denoted by members of the index set $\mathcal{I}_s$, then $i \in \mathcal{I}_s$. A function, called entropy and denoted as $\mathbb{S}$, is described in terms of these variables by a functional form $\mathbb{S}^*$ such that

$$\mathbb{S} = \mathbb{S}^*(\mathbb{E}, \mathbb{V}, \mathbb{M}_1, \mathbb{M}_2, ..., \mathbb{M}_N) \; . \tag{3.1}$$

Further it is assumed that the values assumed by the variables $\mathbb{E}$, $\mathbb{V}$, and $\mathbb{M}_i$ in the absence of constraints are those that maximize $\mathbb{S}$ at equilibrium.

For analysis of multispecies systems, the designation of the string of masses, $\mathbb{M}_1$, $\mathbb{M}_2$, ..., $\mathbb{M}_N$, can become clumsy and, at times, lack precision. This problem will be avoided here by introducing a couple of frequently occurring sets. Let us define the set of all species masses in the entity of interest, $\mathcal{M}$, as

$$\mathcal{M} = \{\mathbb{M}_i | i \in \mathcal{I}_s\} \; , \tag{3.2}$$

where $\mathcal{I}_s$ is the set of species indices $\{1, 2, ..., N\}$. Thus, for example, Eq. (3.1) can be expressed as

$$\mathbb{S} = \mathbb{S}^*(\mathbb{E}, \mathbb{V}, \mathcal{M}) \; . \tag{3.3}$$

The set of all species masses excluding the mass of species i is designated as $\mathcal{M}_i$ and is defined formally as

$$\mathcal{M}_i = \left\{\mathbb{M}_j | (j \in \mathcal{I}_s) \wedge (j \neq i)\right\} \; . \tag{3.4}$$

The set $\mathcal{M}_i$ is convenient when taking derivatives of variables with respect to $\mathbb{M}_i$. Both $\mathcal{M}$ and $\mathcal{M}_i$ will be employed subsequently.

There are three particular attributes of Eq. (3.3) that are important to mention. First, internal energy and entropy are quantities that are presumed to exist. Second, this equation is posed completely in terms of extensive variables, that is variables that are additive when combining systems at the same equilibrium state such that its value is proportional to the size or mass of the system. Extensive variables, such as volume or mass, can be contrasted with intensive variables, such as temperature or mass density, whose values are independent of system extent. The third important point is that Eq. (3.3) applies to fluids at equilibrium. In addition to the definition of equilibrium provided previously relating to time invariance, Callen [8] has provided the noteworthy observation that a system is in an equilibrium state if its properties are consistently described by thermodynamic theory. This observation is somewhat less restrictive than the formal definition of equilibrium in that one might imagine a system whose properties are changing slowly such that they are still described by Eq. (3.3) even though the system is not in an equilibrium state. This final observation will prove important subsequently in the discussion of CIT.

Introduction of $\mathbb{S}$ as function dependent upon a set of extensive variables is mathematically acceptable, but physical intuition is helpful as well. This is not a simple matter in the case of entropy. A common, but flawed, perspective is that entropy is a measure of the disorder in a system. A better definition is that entropy is a measure of the extent to which the energy in a system is distributed over the range of states that are possible. An example that can add some clarity is the case when a gas is confined within a small portion of an isolated system by internal barriers. An isolated system is one that does not allow the exchange of heat or mass across its fixed boundaries. If the internal barriers are removed, the gas will redistribute itself throughout the system. This redistribution results also in a redistribution of energy and an increase in the entropy of the system. When such systems are examined from a molecular viewpoint with statistical mechanics used to relate that viewpoint to the larger scale, it can be shown that entropy is related to the potential number of distributional states of matter at the molecular scale, with the observed state corresponding to the most probable state [e.g., 22].

To arrive at the functional form for entropy, $\mathbb{S}$, one needs to postulate some properties that will be accommodated by the form of the functional relation, $\mathbb{S}^*$. First, we postulate that some extremum properties apply to the fundamental thermodynamic function, namely that in addition to $\mathbb{S}$ being a maximum at equilibrium, $\mathbb{E}$ is a minimum at equilibrium. Second, we postulate that $\mathbb{S}$ for a composite system must be additive over the subsystems and be continuous, differentiable, and a monotonically increasing function of $\mathbb{E}$. These posited conditions are simple and convenient, yet they imply a great deal when exercised in conjunction with Eq. (3.3). Because of the additivity property of all extensive variables, the functional form of $\mathbb{S}^*$ can be ascertained to be a homogeneous first-order function with certain inversion and extremum properties.

The monotonicity between $\mathbb{S}$ and $\mathbb{E}$ and the smoothness property of this relation are such that

$$\left(\frac{\partial \mathbb{S}^*}{\partial \mathbb{E}}\right)_{\mathbb{V},\mathcal{M}} > 0\,. \tag{3.5}$$

The subscripts are employed to indicate explicitly the variables that are being held constant, which is a traditional approach in thermodynamics to ensure that an accurate and precise thermodynamic framework is built upon the posited form of the fundamental function.

Based on Eq. (3.5), Eq. (3.3) can be inverted to obtain an expression for energy as the dependent variable with

$$\mathbb{E} = \mathbb{E}^*(\mathbb{S},\mathbb{V},\mathcal{M})\,. \tag{3.6}$$

We will work primarily with this functional form of the fundamental equation, while noting that the functional form given by Eq. (3.3) is equally valid.

The first-order homogeneous property implies that

$$\lambda \mathbb{E}^{*}(\mathbb{S}, \mathbb{V}, \mathbb{M}_i) = \mathbb{E}^{*}(\lambda \mathbb{S}, \lambda \mathbb{V}, \lambda \mathcal{M}) , \tag{3.7}$$

where λ is any real positive scaling multiplier and $\lambda \mathcal{M}$ indicates that all of the masses in set $\mathcal{M}$ are multiplied by λ. Equation (3.7) can be understood as a logical consequence of the properties of extensive variables that ensure that combined identical systems are additive in terms of their extensive variables; these extensive variables fully specify the thermodynamic state of the system. If the entropy, volume, and masses of chemical species in an equilibrium system are all increased by a factor λ, the energy of the system will also increase by the factor λ.

The change in energy in a system due to differential changes in the independent variables can be examined by computing the first differential of Eq. (3.6), which is

$$\mathrm{d}\mathbb{E} = \left(\frac{\partial \mathbb{E}^{*}}{\partial \mathbb{S}} \right)_{\mathbb{V},\mathcal{M}} \mathrm{d}\mathbb{S} + \left(\frac{\partial \mathbb{E}^{*}}{\partial \mathbb{V}} \right)_{\mathbb{S},\mathcal{M}} \mathrm{d}\mathbb{V} + \sum_{i \in \mathfrak{I}_s} \left(\frac{\partial \mathbb{E}^{*}}{\partial \mathbb{M}_i} \right)_{\mathbb{S},\mathbb{V},\mathcal{M}_i} \mathrm{d}\mathbb{M}_i \, . \tag{3.8}$$

Recall that $\mathcal{M}_i$ is the set of masses of chemical species in the system excluding $\mathbb{M}_i$. The partial derivatives in Eq. (3.8) occur routinely in thermodynamics and out of convenience they are given named symbols to identify the intensive thermodynamic quantities they represent. These are

$$\theta = \left(\frac{\partial \mathbb{E}^{*}}{\partial \mathbb{S}} \right)_{\mathbb{V},\mathcal{M}} , \tag{3.9}$$

$$-p = \left(\frac{\partial \mathbb{E}^{*}}{\partial \mathbb{V}} \right)_{\mathbb{S},\mathcal{M}} , \tag{3.10}$$

and

$$\mu_i = \left(\frac{\partial \mathbb{E}^{*}}{\partial \mathbb{M}_i} \right)_{\mathbb{S},\mathbb{V},\mathcal{M}_i} , \tag{3.11}$$

where θ is the temperature, p is the fluid pressure, and μ_i is the chemical potential of species i. Substitution of Eqs. (3.9)–(3.11) into Eq. (3.8) yields the differential form

$$\mathrm{d}\mathbb{E} = \theta \, \mathrm{d}\mathbb{S} - p \, \mathrm{d}\mathbb{V} + \sum_{i \in \mathfrak{I}_s} \mu_i \, \mathrm{d}\mathbb{M}_i \, . \tag{3.12}$$

Because temperature, pressure, and chemical potential are defined as derivatives of the internal energy, which itself depends on entropy, volume, and species masses, these intensive variables must also each depend on the three extensive independent variable groups, with

$$\theta = \theta_{\mathbb{E}^{*}} (\mathbb{S}, \mathbb{V}, \mathcal{M}) , \tag{3.13}$$

$$p = p_{\mathbb{E}^{*}} (\mathbb{S}, \mathbb{V}, \mathcal{M}) , \tag{3.14}$$

and

$$\mu_i = \mu_{\mathbb{E}^{*} i} (\mathbb{S}, \mathbb{V}, \mathcal{M}) \, . \tag{3.15}$$

The subscript $\mathbb{E}^*$ is used to distinguish formally between an intensive quantity, on the left side of the equation, and the function that describes the intensive quantity on the right. These relations are the equations of state for the formulation in terms of internal energy.

Based on Eqs. (3.5), (3.6), and (3.7), we know that

$$\lambda \mathbb{E} = \mathbb{E}^*(\lambda \mathbb{S}, \lambda \mathbb{V}, \lambda \mathcal{M}) \tag{3.16}$$

and

$$\lambda \mathbb{S} = \mathbb{S}^*(\lambda \mathbb{E}, \lambda \mathbb{V}, \lambda \mathcal{M}) \ . \tag{3.17}$$

Differentiation of Eq. (3.16) gives the equation analogous to Eq. (3.8)

$$\begin{aligned} \mathrm{d}\,(\lambda \mathbb{E}) = {} & \left(\frac{\partial \mathbb{E}^*}{\partial (\lambda \mathbb{S})} \right)_{\lambda \mathbb{V}, \lambda \mathcal{M}} \mathrm{d}\,(\lambda \mathbb{S}) + \left(\frac{\partial \mathbb{E}^*}{\partial (\lambda \mathbb{V})} \right)_{\lambda \mathbb{S}, \lambda \mathcal{M}} \mathrm{d}\,(\lambda \mathbb{V}) \\ & + \sum_{i \in \mathcal{I}_s} \left(\frac{\partial \mathbb{E}^*}{\partial (\lambda \mathbb{M}_i)} \right)_{\lambda \mathbb{S}, \lambda \mathbb{V}, \lambda \mathcal{M}_i} \mathrm{d}\,(\lambda \mathbb{M}_i) \ . \end{aligned} \tag{3.18}$$

Note that all quantities multiplied by λ are extensive quantities. Therefore Eq. (3.18) must apply regardless of the non-zero value of λ. Indeed, Eq. (3.8) is just the special case of Eq. (3.18) when $\lambda = 1$. This also means that we can write more general definitions of temperature, pressure, and chemical potential as

$$\theta = \left(\frac{\partial \mathbb{E}^*}{\partial (\lambda \mathbb{S})} \right)_{\lambda \mathbb{V}, \lambda \mathcal{M}} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{S}} \ , \tag{3.19}$$

$$-p = \left(\frac{\partial \mathbb{E}^*}{\partial (\lambda \mathbb{V})} \right)_{\lambda \mathbb{S}, \lambda \mathcal{M}} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{V}} \ , \tag{3.20}$$

and

$$\mu_i = \left(\frac{\partial \mathbb{E}^*}{\partial (\lambda \mathbb{M}_i)} \right)_{\lambda \mathbb{S}, \lambda \mathbb{V}, \lambda \mathcal{M}_i} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{M}_i} \ , \tag{3.21}$$

where the value of λ is arbitrary. Although the value of λ is arbitrary, some of the definitions given in Eqs. (3.19)–(3.21) cannot be made for some particular choices of λ, as indicated. Furthermore, Eqs. (3.13)–(3.15) can be written in more general forms

$$\theta = \theta_{\mathbb{E}^*}\,(\lambda \mathbb{S}, \lambda \mathbb{V}, \lambda \mathcal{M}) \ , \tag{3.22}$$

$$p = p_{\mathbb{E}^*}\,(\lambda \mathbb{S}, \lambda \mathbb{V}, \lambda \mathcal{M}) \ , \tag{3.23}$$

and

$$\mu_i = \mu_{\mathbb{E}^* i}\,(\lambda \mathbb{S}, \lambda \mathbb{V}, \lambda \mathcal{M}) \ . \tag{3.24}$$

In view of Eqs. (3.22)–(3.24), it follows that rescaling an equilibrium system does not change the values of the intensive thermodynamic quantities. This means that the equations of state for the intensive thermodynamic quantities are homogeneous zero-order equations. Thus while combining two identical systems at equilibrium doubles the internal energy, the entropy, the volume, and mass of each species, this combination leaves temperature, pressure, and chemical potentials unchanged. The intensive thermodynamic variables are unaffected by any combination of identical equilibrium systems. While this has been shown mathematically, it also makes physical sense.

3.3.2 Euler Equation for Internal Energy

The general functional form and the mathematical properties of the fundamental energetic equation of equilibrium thermodynamics can be used to derive an explicit functional form for internal energy. Substitute Eqs. (3.19)–(3.21) into Eq. (3.18) to obtain

$$\mathrm{d}(\lambda\mathbb{E}) = \theta\,\mathrm{d}(\lambda\mathbb{S}) - p\,\mathrm{d}(\lambda\mathbb{V}) + \sum_{i\in\mathfrak{I}_s} \mu_i\,\mathrm{d}(\lambda\mathbb{M}_i)\ . \tag{3.25}$$

Expansion of the differentials using the product rule then yields

$$\begin{aligned}\mathbb{E}\,\mathrm{d}\lambda + \lambda\,\mathrm{d}\mathbb{E} =& \lambda\left(\theta\,\mathrm{d}\mathbb{S} - p\,\mathrm{d}\mathbb{V} + \sum_{i\in\mathfrak{I}_s} \mu\,\mathrm{d}\mathbb{M}_i\right)\\ &+\left(\theta\mathbb{S} - p\mathbb{V} + \sum_{i\in\mathfrak{I}_s} \mu_i\mathbb{M}_i\right)\mathrm{d}\lambda\ .\end{aligned} \tag{3.26}$$

The terms multiplied by λ, the second term on the left and the first group of terms in parentheses on the right, cancel according to Eq. (3.12), leaving

$$\mathbb{E}\,\mathrm{d}\lambda = \left(\theta\mathbb{S} - p\mathbb{V} + \sum_{i\in\mathfrak{I}_s} \mu_i\mathbb{M}_i\right)\mathrm{d}\lambda\ . \tag{3.27}$$

Because $\mathrm{d}\lambda$ is arbitrary, the quantities on the left and right sides of this equation that multiply $\mathrm{d}\lambda$ must be equal to preserve the equality such that

$$\mathbb{E} = \theta\mathbb{S} - p\mathbb{V} + \sum_{i\in\mathfrak{I}_s} \mu_i\mathbb{M}_i\ . \tag{3.28}$$

Equation (3.28) is called the *Euler equation* for the internal energy of a fluid phase.

Equation (3.28) is a very important equation. It provides the explicit form for internal energy, which was originally only posited in the fundamental functional form of Eq. (3.6). Because Eqs. (3.13)–(3.15) indicate that θ, p, and μ_i for all i are functions of $\mathbb{S}$, $\mathbb{V}$, and $\mathcal{M}$, the internal energy itself is confirmed as being a function only of these extensive variables that fully specify the thermodynamic state of a system.

One other important expression that results from Eqs. (3.16), (3.17), and (3.25) is the heat capacity at constant volume and composition, $\mathbb{C}_V$, which is defined as

$$\lambda \mathbb{C}_V = \left(\frac{\partial \mathbb{E}^*}{\partial \theta} \right)_{\lambda \mathbb{V}, \lambda \mathcal{M}} = \theta \left(\frac{\partial \mathbb{S}^*}{\partial \theta} \right)_{\lambda \mathbb{V}, \lambda \mathcal{M}} . \tag{3.29}$$

Selection of $\lambda = 1$ gives the extensive heat capacity as the energy per unit of temperature.

3.3.3 Gibbs-Duhem Equation for a Fluid

In addition to the Euler equation as provided by Eq. (3.28) and the differential relation for internal energy in Eq. (3.12), there is a third fundamental equation of importance, the *Gibbs-Duhem equation.* This equation is readily derived.

First, take the differential of Eq. (3.28) to obtain

$$\mathrm{d}\mathbb{E} = \theta \,\mathrm{d}\mathbb{S} + \mathbb{S}\,\mathrm{d}\theta - p\,\mathrm{d}\mathbb{V} - \mathbb{V}\,\mathrm{d}p + \sum_{i \in \mathcal{I}_s} \left(\mu_i \,\mathrm{d}\mathbb{M}_i + \mathbb{M}_i \,\mathrm{d}\mu_i \right) . \tag{3.30}$$

Equation (3.12) can then be applied to this expression to eliminate the terms involving $\mathrm{d}\mathbb{E}$, $\mathrm{d}\mathbb{S}$, $\mathrm{d}\mathbb{V}$, and $\mathrm{d}\mathbb{M}_i$, leaving

$$0 = \mathbb{S}\,\mathrm{d}\theta - \mathbb{V}\,\mathrm{d}p + \sum_{i \in \mathcal{I}_s} \mathbb{M}_i \,\mathrm{d}\mu_i , \tag{3.31}$$

which is the Gibbs-Duhem equation.

The Gibbs-Duhem equation expresses a differential equality among the changes in intensive variables that must exist within a system when moving from one equilibrium state to a second equilibrium state. The fact that Eq. (3.31) provides a means for relating the change in some set of intensive variables to a remaining set of intensive variables will prove to be of significant value in the development of TCAT models. It also serves as a constraint ensuring that variables designated as “temperature” or “pressure” at some larger scale are well defined such that they are constrained by the requirements of the Gibbs-Duhem equation.

Some caution is needed in the use of the Gibbs-Duhem equation. One might be inclined to solve this differential equation for one missing equation of state through integration when the other equations of state are known. However, this approach introduces a constant of integration that is unresolved. This should not be surprising because complete specification of the Euler equation requires identification of all equations of state for a system. If one equation of state is unknown, the Euler equation can only be specified within a constant. However, the Euler equation along with its three associated equations of state completely specifies the thermodynamic properties of a system.

3.4 Normalized Internal Energy Formulation

Eq. (3.28) is the explicit form of the internal energy function given in Eq. (3.6). Alternatively, it can be thought of as the explicit form of Eq. (3.16) with $\lambda = 1$. Thus, with the general coefficient λ included in the energy statements, we have the expressions given, respectively, as Eqs. (3.16) and (3.25),

$$\lambda \mathbb{E} = \mathbb{E}^*(\lambda \mathbb{S}, \lambda \mathbb{V}, \lambda \mathcal{M}) \tag{3.32}$$

and

$$\mathrm{d}(\lambda \mathbb{E}) = \theta \, \mathrm{d}(\lambda \mathbb{S}) - p \, \mathrm{d}(\lambda \mathbb{V}) + \sum_{i \in \mathfrak{I}_s} \mu_i \, \mathrm{d}(\lambda \mathbb{M}_i) \ . \tag{3.33}$$

Two other equations can be obtained to complete the set by multiplying the Euler equation and the Gibbs-Duhem equation, Eqs. (3.28) and (3.31) respectively, by λ such that

$$\lambda \mathbb{E} = \theta \lambda \mathbb{S} - p \lambda \mathbb{V} + \sum_{i \in \mathfrak{I}_s} \mu_i \lambda \mathbb{M}_i \tag{3.34}$$

and

$$0 = \lambda \mathbb{S} \, \mathrm{d}\theta - \lambda \mathbb{V} \, \mathrm{d}p + \sum_{i \in \mathfrak{I}_s} \lambda \mathbb{M}_i \, \mathrm{d}\mu_i \ . \tag{3.35}$$

At the risk of redundancy, we emphasize that these expressions apply to equilibrium systems that have uniform properties and that Eq. (3.33) applies to differential changes in variables associated with a change in equilibrium states.

It has been stated previously that λ is a positive, real, scaling multiplier. Although Eqs. (3.32)–(3.35) are written with extensive independent variables, it is sometimes more convenient to work in terms of these extensive variables normalized by a certain quantity. For instance, the conservation of energy equation for a phase is written in terms of the internal energy per volume, and it is useful to be able to relate this quantity to a thermodynamic expression. By judicious selection of λ, the expressions can be made applicable for describing the system behavior in terms of densities of the extensive variables or values of the variables per unit mass. Some instances are demonstrated here, although we note that selection of a value of λ is not restricted to the physically convenient values employed.

As a first example, select $\lambda = 1/\mathbb{V}$. Then Eqs. (3.32)–(3.35) become, respectively

$$\frac{\mathbb{E}}{\mathbb{V}} = \mathbb{E}^*(\frac{\mathbb{S}}{\mathbb{V}}, \frac{\mathbb{V}}{\mathbb{V}}, \frac{\mathcal{M}}{\mathbb{V}}) \ , \tag{3.36}$$

$$\mathrm{d}\left(\frac{\mathbb{E}}{\mathbb{V}}\right) = \theta \, \mathrm{d}\left(\frac{\mathbb{S}}{\mathbb{V}}\right) - p \, \mathrm{d}\left(\frac{\mathbb{V}}{\mathbb{V}}\right) + \sum_{i \in \mathfrak{I}_s} \mu_i \, \mathrm{d}\left(\frac{\mathbb{M}_i}{\mathbb{V}}\right) \ , \tag{3.37}$$

$$\frac{\mathbb{E}}{\mathbb{V}} = \theta \frac{\mathbb{S}}{\mathbb{V}} - p \frac{\mathbb{V}}{\mathbb{V}} + \sum_{i \in \mathfrak{I}_s} \mu_i \frac{\mathbb{M}_i}{\mathbb{V}} \ , \tag{3.38}$$

and

$$0 = \frac{\mathbb{S}}{\mathbb{V}}\,\mathrm{d}\theta - \frac{\mathbb{V}}{\mathbb{V}}\,\mathrm{d}p + \sum_{i\in\mathcal{I}_s} \frac{\mathbb{M}_i}{\mathbb{V}}\,\mathrm{d}\mu_i\ . \tag{3.39}$$

Because the equilibrium variables are uniform, $\mathbb{E}/\mathbb{V}$ can be replaced by the energy per volume, E, $\mathbb{S}/\mathbb{V}$ can be replaced by the entropy per volume, η, and $\mathbb{M}_i/\mathbb{V}$ is equal to the mass of species i per volume, written as $\rho\omega_i$ where ρ is the mass per volume and ω_i is the mass fraction of species i. Note that $\mathbb{V}/\mathbb{V} = 1$ and its derivative is zero. Thus the thermodynamic equations in terms of energy per volume simplify to

$$E = \mathbb{E}^*(\eta, 1, \mathcal{R})\ , \tag{3.40}$$

$$\mathrm{d}E = \theta\,\mathrm{d}\eta + \sum_{i\in\mathcal{I}_s} \mu_i\,\mathrm{d}(\rho\omega_i)\ , \tag{3.41}$$

$$E = \theta\eta - p + \sum_{i\in\mathcal{I}_s} \mu_i\rho\omega_i\ , \tag{3.42}$$

and

$$0 = \eta\,\mathrm{d}\theta - \mathrm{d}p + \sum_{i\in\mathcal{I}_s} \rho\omega_i\,\mathrm{d}\mu_i\ , \tag{3.43}$$

where $\mathcal{R}$ is the set of masses per volume of the chemical species such that

$$\mathcal{R} = \{\rho\omega_i | i \in \mathcal{I}_s\}\ . \tag{3.44}$$

This equation set has several interesting features. Equation (3.40) provides the fact that the functional form given as $\mathbb{E}^*$ is the same for both $\mathbb{E}$ and E, although the independent variables that appear are different. For E as opposed to $\mathbb{E}$, there is one less independent variable (i.e., $\mathbb{V}$ is replaced by 1), and the entropy density and mass densities of the species replace entropy and mass of the species. From Eq. (3.41) we obtain definitions of temperature and chemical potential, respectively, making use of Eq. (3.40), as

$$\theta = \left(\frac{\partial\mathbb{E}^*}{\partial\eta}\right)_{\mathcal{R}} \tag{3.45}$$

and

$$\mu_i = \left(\frac{\partial\mathbb{E}^*}{\partial(\rho\omega_i)}\right)_{\eta,\mathcal{R}_i}\ . \tag{3.46}$$

where, analogously to $\mathcal{M}_i$ defined in Eq. (3.4), $\mathcal{R}_i$ is defined as

$$\mathcal{R}_i = \{\rho\omega_j | (j \in \mathcal{I}_s) \wedge (j \neq i)\}\ . \tag{3.47}$$

These definitions of θ and μ_i are equivalent to those given in Eqs. (3.9) and (3.11) (or Eqs. (3.19) and (3.21) with $\lambda = 1/\mathbb{V}$). However, no definition of pressure is obtained as a partial of the internal energy function that is analogous to Eq. (3.10) or Eq. (3.20). This can be understood, perhaps most easily, with reference to Eq. (3.20). If one sets $\lambda = 1/\mathbb{V}$ in this equation, the differentiation is with respect to a constant, which is meaningless. Although pressure is not obtained as a partial derivative of energy density with respect to some quantity, the equation set Eqs. (3.40)–(3.43) is still applicable to the case where the system volume is varying.

Equations of state for the intensive variables have been provided in Eqs. (3.22)–(3.24) where λ may be selected arbitrarily. If $\lambda = 1$, the intensive state variables are dependent on the extensive variables, $\mathbb{S}$, $\mathbb{V}$, and $\mathcal{M}$. However, if $\lambda = 1/\mathbb{V}$, the equations of state become

$$\theta = \theta_{\mathbb{E}^*}(\eta, 1, \mathcal{R}) \;, \tag{3.48}$$

$$p = p_{\mathbb{E}^*}(\eta, 1, \mathcal{R}) \;, \tag{3.49}$$

and

$$\mu_i = \mu_{\mathbb{E}^*i}(\eta, 1, \mathcal{R}) \;. \tag{3.50}$$

Thus, the number of independent variables is reduced by one.

In some instances, it may be convenient to work with energy per mass. Equations for this situation are obtained directly from Eqs. (3.32)–(3.35) by selecting $\lambda = 1/\mathbb{M}$. Because this text makes use of energy density in preference to energy per mass, the calculations are not provided here. However, they are encouraged in the exercises at the end of the chapter.

3.5 Other Thermodynamic Potentials

Thermodynamics involves studying the equilibrium state of a system based upon the values of a set of independent variables. When the independent variables are $\mathbb{S}$, $\mathbb{V}$, and $\mathcal{M}$, the fundamental form of internal energy, $\mathbb{E}$, can be specified. Although specification of these variables determines the energy, equations of state are also needed for $\theta(\mathbb{S}, \mathbb{V}, \mathcal{M})$, $p(\mathbb{S}, \mathbb{V}, \mathcal{M})$, and $\mu_i(\mathbb{S}, \mathbb{V}, \mathcal{M})$ to complete the evaluation of the internal energy in conjunction with an Euler equation. Unfortunately, control of the independent variables, particularly $\mathbb{S}$, may be experimentally difficult or inconvenient. Thus, supporting experimental measurements can be simplified by controlling variables other than the natural independent variables for internal energy. For easiest coordination of these experiments with thermodynamic relations, a transformation of variables can be employed that does not lose any information contained in the fundamental form for $\mathbb{E}$ along with the equations of state. A range of useful alternative energy forms, or potentials, can be derived in a general context using Legendre transformations [8]. Here, we will adopt a less elegant and general approach in the interest of brevity but will develop the Helmholtz free energy, enthalpy, and the Gibbs free energy potentials.

3.5.1 Helmholtz Free Energy

Start with defining a new energy function, $\mathbb{F}$, referred to as the Helmholtz potential or Helmholtz free energy, according to

$$\lambda\mathbb{F} = \lambda\mathbb{E} - \theta\lambda\mathbb{S} \,. \tag{3.51}$$

Note that λ is carried along simply to facilitate development of subsequent expressions. The differential of Eq. (3.51) is

$$\mathrm{d}\,(\lambda\mathbb{F}) = \mathrm{d}\,(\lambda\mathbb{E}) - \theta\,\mathrm{d}\,(\lambda\mathbb{S}) - \lambda\mathbb{S}\,\mathrm{d}\theta \,. \tag{3.52}$$

Substitution of Eq. (3.33) into this expression to eliminate $\mathrm{d}\,(\lambda\mathbb{E})$ and cancellation of the terms involving $\theta\,\mathrm{d}\,(\lambda\mathbb{S})$ yields

$$\mathrm{d}\,(\lambda\mathbb{F}) = -\lambda\mathbb{S}\,\mathrm{d}\theta - p\,\mathrm{d}\,(\lambda\mathbb{V}) + \sum_{i\in\mathfrak{I}_s} \mu_i\,\mathrm{d}\,(\lambda\mathbb{M}_i) \,. \tag{3.53}$$

This expression of the differential means that $\lambda\mathbb{F}$ is fundamentally a function of θ, $\lambda\mathbb{V}$, and $\lambda\mathcal{M}$ that can be expressed as

$$\lambda\mathbb{F} = \mathbb{F}^*\left(\theta, \lambda\mathbb{V}, \lambda\mathcal{M}\right) \,, \tag{3.54}$$

where $\mathbb{F}^*$ is the functional form, with

$$-\lambda\mathbb{S} = \left(\frac{\partial\mathbb{F}^*}{\partial\theta}\right)_{\lambda\mathbb{V},\lambda\mathcal{M}} \,, \tag{3.55}$$

$$-p = \left(\frac{\partial\mathbb{F}^*}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{V}} \,, \tag{3.56}$$

and

$$\mu_i = \left(\frac{\partial\mathbb{F}^*}{\partial(\lambda\mathbb{M}_i)}\right)_{\theta,\lambda\mathbb{V},\lambda\mathcal{M}_i} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{M}_i} \,. \tag{3.57}$$

Additionally, the Euler form of the Helmholtz free energy function may be obtained by substituting Eq. (3.28) into Eq. (3.51) to eliminate $\mathbb{E}$, leaving

$$\lambda\mathbb{F} = -p\lambda\mathbb{V} + \sum_{i\in\mathfrak{I}_s} \mu_i\lambda\mathbb{M}_i \,. \tag{3.58}$$

The preceding essentially defines an energy potential wherein the independent variable $\mathbb{S}$ is replaced by θ. The validity of this transformation requires that θ be a monotonic function of $\mathbb{S}$ such that their functional dependence can be inverted. If the transformation is allowable, the defined Helmholtz potential function, plus its corresponding equations of state, contains the complete information of the system, just as the internal energy function contains complete information. The benefit of working with $\mathbb{F}$ rather than $\mathbb{E}$ is that temperature, as an independent variable, is easier to control and observe than entropy in an experimental setting. The equations of state for the derived variables in Eqs. (3.55)–(3.57) are expressed as

$$\lambda\mathbb{S} = \mathbb{S}_{\mathbb{F}^*}\left(\theta, \lambda\mathbb{V}, \lambda\mathcal{M}\right) , \tag{3.59}$$

$$p = p_{\mathbb{F}^*}\left(\theta, \lambda\mathbb{V}, \lambda\mathcal{M}\right) , \tag{3.60}$$

and

$$\mu_i = \mu_{\mathbb{F}^*i}\left(\theta, \lambda\mathbb{V}, \lambda\mathcal{M}\right) , \tag{3.61}$$

where the subscript $\mathbb{F}^*$ is used to distinguish the functional form from the variable and to emphasize that the equations of state here are those associated with the Helmholtz free energy rather than those associated with the internal energy given by Eqs. (3.22)–(3.24). We note that although the functional forms and dependences of variables are different, the meaning and values of the variables themselves are not changed.

By selecting $\lambda = 1$ in the preceding equations, we will obtain the thermodynamic expressions for the Helmholtz energy of a system at equilibrium. Here, with an eye toward applicability in TCAT modeling, we will select $\lambda = 1/\mathbb{V}$ to obtain expressions for the Helmholtz potential per unit volume denoted as F. From Eqs. (3.54), (3.58), and (3.53), respectively, we obtain the fundamental functional dependence of F, its Euler form, and its differential as

$$F = \mathbb{F}^*\left(\theta, 1, \mathcal{R}\right) , \tag{3.62}$$

$$F = -p + \sum_{i\in\mathfrak{I}_s} \mu_i \rho\omega_i , \tag{3.63}$$

and

$$\mathrm{d}F = -\eta\,\mathrm{d}\theta + \sum_{i\in\mathfrak{I}_s} \mu_i\,\mathrm{d}\left(\rho\omega_i\right) . \tag{3.64}$$

In terms of derivatives of the functional form of F, the entropy and chemical potential are obtained from Eqs. (3.55) and (3.57) with $\lambda = 1/\mathbb{V}$ as

$$-\eta = \left(\frac{\partial\mathbb{F}^*}{\partial\theta}\right)_{\mathcal{R}} \tag{3.65}$$

and

$$\mu_i = \left(\frac{\partial\mathbb{F}^*}{\partial\left(\rho\omega_i\right)}\right)_{\theta,\mathcal{R}_i} . \tag{3.66}$$

Finally, the state equations for entropy per volume, pressure, and chemical potential follow directly from Eqs. (3.59)–(3.61) in the forms

$$\eta = \mathbb{S}_{\mathbb{F}^*}\left(\theta, 1, \mathcal{R}\right) , \tag{3.67}$$

$$p = p_{\mathbb{F}^*}\left(\theta, 1, \mathcal{R}\right) , \tag{3.68}$$

and

$$\mu_i = \mu_{\mathbb{F}^*i}(\theta, 1, \mathcal{R}) \ . \tag{3.69}$$

Note that for the case where the fluid phase is composed of a single chemical constituent, $\mathcal{R} = \{\rho\}$; and the state equations provide variables as functions of temperature and density.

3.5.2 Enthalpy

Another energy function that is commonly employed is the enthalpy, $\mathbb{H}$, defined as

$$\lambda\mathbb{H} = \lambda\mathbb{E} + p\lambda\mathbb{V} \ . \tag{3.70}$$

The differential of this expression is

$$\mathrm{d}(\lambda\mathbb{H}) = \mathrm{d}(\lambda\mathbb{E}) + p\,\mathrm{d}(\lambda\mathbb{V}) + \lambda\mathbb{V}\,\mathrm{d}p \ . \tag{3.71}$$

Substitution of Eq. (3.33) into Eq. (3.71) to eliminate $\mathrm{d}(\lambda\mathbb{E})$ and cancellation of the terms involving $p\,\mathrm{d}(\lambda\mathbb{V})$ yield

$$\mathrm{d}(\lambda\mathbb{H}) = \theta\,\mathrm{d}(\lambda\mathbb{S}) + \lambda\mathbb{V}\,\mathrm{d}p + \sum_{i\in\mathcal{I}_s} \mu_i\,\mathrm{d}(\lambda\mathbb{M}_i) \ . \tag{3.72}$$

This expression of the exact differential shows that $\lambda\mathbb{H}$ is a function of $\lambda\mathbb{S}$, p, and $\lambda\mathcal{M}$. Thus, the fundamental functional dependence of $\lambda\mathbb{H}$ is

$$\lambda\mathbb{H} = \mathbb{H}^*(\lambda\mathbb{S}, p, \lambda\mathcal{M}) \ , \tag{3.73}$$

where $\mathbb{H}^*$ is a functional form, and

$$\theta = \left(\frac{\partial\mathbb{H}^*}{\partial(\lambda\mathbb{S})}\right)_{p,\lambda\mathcal{M}} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{S}} \ , \tag{3.74}$$

$$\lambda\mathbb{V} = \left(\frac{\partial\mathbb{H}^*}{\partial p}\right)_{\lambda\mathbb{S},\lambda\mathcal{M}} \ , \tag{3.75}$$

and

$$\mu_i = \left(\frac{\partial\mathbb{H}^*}{\partial(\lambda\mathbb{M}_i)}\right)_{\lambda\mathbb{S},p,\lambda\mathcal{M}_i} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{M}_i} \ . \tag{3.76}$$

Note that if we invert Eq. (3.73), an alternative functional form to Eq. (3.17) for the entropy is

$$\lambda\mathbb{S} = \mathbb{S}^*_{\mathbb{H}}(\lambda\mathbb{H}, p, \lambda\mathcal{M}) \ . \tag{3.77}$$

Additionally, substitution of Eq. (3.28) into Eq. (3.70) to eliminate $\lambda\mathbb{E}$ yields the Euler form of the enthalpy,

$$\lambda\mathbb{H} = \theta\lambda\mathbb{S} + \sum_{i\in\mathfrak{I}_s} \mu_i\lambda\mathbb{M}_i \ . \tag{3.78}$$

The manipulations in this section have led to an energy potential, enthalpy, that in comparison with the internal energy makes use of p as a fundamental independent variable rather than $\lambda\mathbb{V}$. The validity of this transformation requires that p be a monotonic function of $\lambda\mathbb{V}$ such that their functional dependence can be inverted. If the transformation is allowable, the defined fundamental enthalpy function with its associated equations of state contains the complete information of the system, in the same way that the internal energy function, along with its associated state equations, contains complete information. The utility of the enthalpy is in describing or making measurements of systems where p rather than $\mathbb{V}$ is held constant such that $\mathbb{H}$ is easier to work with than $\mathbb{E}$. The equations of state for the derived variables in Eqs. (3.74)–(3.76) are

$$\theta = \theta_{\mathbb{H}^*}\left(\lambda\mathbb{S}, p, \lambda\mathcal{M}\right) \ , \tag{3.79}$$

$$\lambda\mathbb{V} = \mathbb{V}_{\mathbb{H}^*}\left(\lambda\mathbb{S}, p, \lambda\mathcal{M}\right) \ , \tag{3.80}$$

and

$$\mu_i = \mu_{\mathbb{H}^*i}\left(\lambda\mathbb{S}, p, \lambda\mathcal{M}\right) \ . \tag{3.81}$$

Here the subscript $\mathbb{H}^*$ is used to distinguish the functional form from the variable and from other state equations for the dependent variable written in terms of different independent variables (e.g., Eqs. (3.22)–(3.24)). Although the equations of state are written with different functional dependences, all variables appearing in equations of state have the same meaning and values regardless of which energy function is being discussed.

Selection of $\lambda = 1$ in the preceding equations provides the thermodynamic expressions for the enthalpy of a system at equilibrium. Here we will provide the equations that result when $\lambda = 1/\mathbb{V}$ as the enthalpy density is more useful for TCAT purposes. The enthalpy per volume is denoted as H. From Eqs. (3.73), (3.78), and (3.72), respectively, we obtain the expressions for the functional dependence of H, its Euler form, and its differential as

$$H = \mathbb{H}^*\left(\eta, p, \mathcal{R}\right) \ , \tag{3.82}$$

$$H = \theta\eta + \sum_{i\in\mathfrak{I}_s} \mu_i\rho\omega_i \ , \tag{3.83}$$

and

$$\mathrm{d}H = \theta\,\mathrm{d}\eta + \mathrm{d}p + \sum_{i\in\mathfrak{I}_s} \mu_i\,\mathrm{d}\left(\rho\omega_i\right) \ . \tag{3.84}$$

In terms of derivatives of the functional form of H, the temperature and chemical potential are obtained from Eqs. (3.74) and (3.76) as

$$\theta = \left(\frac{\partial\mathbb{H}^*}{\partial\eta}\right)_{p,\mathcal{R}} \tag{3.85}$$

and

$$\mu_i = \left(\frac{\partial \mathbb{H}^*}{\partial (\rho \omega_i)} \right)_{\eta, p, \mathcal{R}_i} . \tag{3.86}$$

Finally, the state equations for temperature and chemical potential follow directly from Eqs. (3.79) and (3.81) in the forms

$$\theta = \theta_{\mathbb{H}^*} (\eta, p, \mathcal{R}) \tag{3.87}$$

and

$$\mu_i = \mu_{\mathbb{H}^* i} (\eta, p, \mathcal{R}) \ . \tag{3.88}$$

Note that with $\lambda = 1/\mathbb{V}$, Eq. (3.75) may be integrated directly to obtain

$$\mathbb{H}^* (\eta, p, \mathcal{R}) = p + f (\eta, \mathcal{R}) \ , \tag{3.89}$$

where f is a function of integration. From Eq. (3.70) with $\lambda = 1/\mathbb{V}$ and Eq. (3.40) it is clear that

$$f (\eta, \mathcal{R}) = \mathbb{E}^* (\eta, 1, \mathcal{R}) \ . \tag{3.90}$$

Thus, Eq. (3.80) does not actually provide an additional state equation when $\lambda = 1/\mathbb{V}$ as it only provides redundancy of the definition of enthalpy.

The enthalpy function is also used as a basis for defining the general heat capacity at constant pressure and composition, $\mathbb{C}_P$. Based on Eqs. (3.72), (3.73), and (3.77), we obtain the definitions

$$\lambda \mathbb{C}_P = \left(\frac{\partial \mathbb{H}^*}{\partial \theta} \right)_{p, \lambda \mathcal{M}} = \theta \left(\frac{\partial \mathbb{S}^*_{\mathbb{H}}}{\partial \theta} \right)_{p, \lambda \mathcal{M}} . \tag{3.91}$$

Selection of $\lambda = 1$ gives the extensive heat capacity for a constant pressure process while selection of $\lambda = 1/\mathbb{V}$ gives the heat capacity at constant pressure per unit volume.

3.5.3 Gibbs Free Energy

The introduction of the Helmholtz free energy and the enthalpy in the preceding sections involved a change in a single independent variable, from entropy to temperature for Helmholtz free energy and from volume to pressure for the enthalpy. Another option is to introduce an energy measure that involves a change in both these variables. This measure is the Gibbs free energy, $\mathbb{G}$, defined by

$$\lambda \mathbb{G} = \lambda \mathbb{E} - \theta \lambda \mathbb{S} + p \lambda \mathbb{V} \ . \tag{3.92}$$

If we take the differential of this expression and substitute in Eq. (3.33) to eliminate $\mathrm{d}(\lambda \mathbb{E})$, the differential of the Gibbs free energy is obtained as

$$\mathrm{d}(\lambda\mathbb{G}) = -\lambda\mathbb{S}\,\mathrm{d}\theta + \lambda\mathbb{V}\,\mathrm{d}p + \sum_{i\in\mathcal{I}_s} \mu_i\,\mathrm{d}(\lambda\mathbb{M}_i)\ . \tag{3.93}$$

Because this is an exact differential form, the general functional form of $\lambda\mathbb{G}$ is

$$\lambda\mathbb{G} = \mathbb{G}^*(\theta, p, \lambda\mathcal{M})\ , \tag{3.94}$$

where $\mathbb{G}^*$ is a functional form subject to

$$-\lambda\mathbb{S} = \left(\frac{\partial\mathbb{G}^*}{\partial\theta}\right)_{p,\lambda\mathcal{M}}\ , \tag{3.95}$$

$$\lambda\mathbb{V} = \left(\frac{\partial\mathbb{G}^*}{\partial p}\right)_{\theta,\lambda\mathcal{M}}\ , \tag{3.96}$$

and

$$\mu_i = \left(\frac{\partial\mathbb{G}^*}{\partial(\lambda\mathbb{M}_i)}\right)_{\theta,p,\lambda\mathcal{M}_i} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{M}_i}\ . \tag{3.97}$$

Substitution of Eq. (3.28) into Eq. (3.92) to eliminate $\lambda\mathbb{E}$ yields the Euler form of the Gibbs free energy,

$$\lambda\mathbb{G} = \sum_{i\in\mathcal{I}_s} \mu_i\lambda\mathbb{M}_i\ . \tag{3.98}$$

The Gibbs free energy is convenient to work with in an experimental setting since pressure and temperature are independent variables, and these are relatively easy to control and monitor. The transformation from internal energy to Gibbs free energy requires smoothness of the relation between the pairs of interchanged variables. If the transformation is allowable, the Gibbs free energy with the equations of state contains the complete information of the system. The equations of state for the derived variables in Eqs. (3.95)–(3.97) are then

$$\lambda\mathbb{S} = \mathbb{S}_{\mathbb{G}^*}(\theta, p, \lambda\mathcal{M})\ , \tag{3.99}$$

$$\lambda\mathbb{V} = \mathbb{V}_{\mathbb{G}^*}(\theta, p, \lambda\mathcal{M})\ , \tag{3.100}$$

and

$$\mu_i = \mu_{\mathbb{G}^*i}(\theta, p, \lambda\mathcal{M})\ . \tag{3.101}$$

Here the subscript $\mathbb{G}^*$ indicates that these equations of state are written in terms of the natural independent variables of the Gibbs free energy.

Selection of $\lambda = 1$ in the preceding equations provides the thermodynamic expressions for the Gibbs free energy of a system at equilibrium. Here we will provide the equations that result when $\lambda = 1/\mathbb{V}$. The Gibbs free energy per volume is denoted as $G = \mathbb{G}/\mathbb{V}$. From Eqs. (3.94), (3.98), and (3.93), respectively, we obtain the expressions for the functional dependence of G, its Euler form, and its differential as

$$G = \mathbb{G}^*(\theta, p, \mathcal{R})\ , \tag{3.102}$$

$$G = \sum_{i \in \mathfrak{I}_s} \mu_i \rho \omega_i \ , \tag{3.103}$$

and

$$\mathrm{d}G = -\eta \, \mathrm{d}\theta + \mathrm{d}p + \sum_{i \in \mathfrak{I}_s} \mu_i \, \mathrm{d}\left(\rho \omega_i\right) \ . \tag{3.104}$$

Expressions for the entropy per volume and the chemical potential obtained from Eqs. (3.95) and (3.97) are

$$-\eta = \left(\frac{\partial \mathbb{G}^*}{\partial \theta} \right)_{p,\mathcal{R}} \tag{3.105}$$

and

$$\mu_i = \left(\frac{\partial \mathbb{G}^*}{\partial (\rho \omega_i)} \right)_{\theta,p,\mathcal{R}_i} \ . \tag{3.106}$$

Finally, the state equations for entropy per volume and chemical potential follow directly from Eqs. (3.79)–(3.81) with the dependence given by the forms

$$\eta = \eta_{\mathbb{G}^*}\left(\theta, p, \mathcal{R}\right) \tag{3.107}$$

and

$$\mu_i = \mu_{\mathbb{G}^* i}\left(\theta, p, \mathcal{R}\right) \ . \tag{3.108}$$

Similarly to H, only two equations of state are needed in considering G, while the number of independent variables in the expression for G is one more than for E and F.

3.5.4 Comments on Energy Potentials

In the preceding definitions of potentials, we have expressed each potential in terms of a different set of independent variables. For example, E depends on η and $\mathcal{R}$ while F depends on θ and $\mathcal{R}$. These are the fundamental dependences that, in concert with associated state equations, contain all the thermodynamic information about the system. However, since θ depends on η and $\mathcal{R}$ as given by equation of state Eq. (3.48), it is possible to alternatively express E as a function of θ and $\mathcal{R}$. Callen [8] points out, however, that such an alternative is not a fundamental relation as it does not contain all possible thermodynamic information about the system. This is one of the reasons that it is important to identify the variables being held constant when differentiating a thermodynamic potential with respect to an independent variable. It is for this reason that functions with an asterisk were used to explicitly denote the functional dependence being employed in the relations in this section. The energy potentials that have been discussed here are all expressed in terms of their associated fundamental independent variables.

One must also be careful in working with potentials scaled by λ in contrast to the extensive variables. For example, pressure is defined as the negative of the partial of $\mathbb{F}$ with respect to volume while holding temperature and the masses of the chemical species constant. However, if one is writing relations in terms of Helmholtz free energy per volume, F, no corresponding differentiation exists that defines the pressure. However, if one is working with Helmholtz free energy per mass, obtained by setting $\lambda = 1/\mathbb{M}$ where $\mathbb{M}$ is the mass of the system, then a definition of pressure in terms of a differential of this function can be obtained. This point is explored further in the exercises at the end of the chapter.

An extremely important principle that must be observed when working with thermodynamic relations is to be careful and clear in identifying functions and independent variables. Without observing this principle, one can be in a position of making alternative definitions of intensive variables in ways that are inconsistent with each other. For example, stating that temperature is the partial of internal energy with respect to entropy is correct only if one states that the volume and masses of each component of the system are being held constant. The partial derivative of internal energy with respect to entropy while holding pressure and masses constant is not equal to the temperature. In the next section we will reinforce the important nature of the explicit listing and accounting for functional dependence.

3.6 Relation between $\mathbb{C}_P$ and $\mathbb{C}_V$

To determine the relation between forms of the heat capacity, one can make use of equations of state that arise when writing the various forms of the energy potentials. For example, in formulating the Helmholtz free energy, we obtained the equation of state for the entropy in Eq. (3.59). The differential of this expression is

$$\mathrm{d}(\lambda\mathbb{S}) = \left(\frac{\partial \mathbb{S}_{\mathbb{F}^*}}{\partial \theta}\right)_{\lambda\mathbb{V},\lambda\mathcal{M}} \mathrm{d}\theta + \left(\frac{\partial \mathbb{S}_{\mathbb{F}^*}}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} \mathrm{d}(\lambda\mathbb{V}) + \sum_{i\in\mathcal{I}_s} \left(\frac{\partial \mathbb{S}_{\mathbb{F}^*}}{\partial(\lambda\mathbb{M}_i)}\right)_{\theta,\lambda\mathbb{V},\lambda\mathcal{M}_i} \mathrm{d}(\lambda\mathbb{M}_i)\ . \tag{3.109}$$

Equation (3.29) defines $\mathbb{C}_V$ in terms of the partial of $\mathbb{S}^*$ with respect to temperature. However, any functional form of entropy is still the entropy. Therefore, the partial derivative in the first term in Eq. (3.109) is equal to $\lambda\mathbb{C}_V/\theta$ and we obtain

$$\mathrm{d}(\lambda\mathbb{S}) = \frac{\lambda\mathbb{C}_V}{\theta}\mathrm{d}\theta + \left(\frac{\partial \mathbb{S}_{\mathbb{F}^*}}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} \mathrm{d}(\lambda\mathbb{V}) + \sum_{i\in\mathcal{I}_s} \left(\frac{\partial \mathbb{S}_{\mathbb{F}^*}}{\partial(\lambda\mathbb{M}_i)}\right)_{\theta,\lambda\mathbb{V},\lambda\mathcal{M}_i} \mathrm{d}(\lambda\mathbb{M}_i)\ . \tag{3.110}$$

This differential of $\lambda\mathbb{S}$ can be examined further by making it with respect to θ while holding p and $\lambda\mathcal{M}$ constant. These conditions were selected with an eye toward getting a desired form for the derivative of $\lambda\mathbb{S}$. If we apply these conditions, Eq.

(3.110) becomes

$$\left(\frac{\partial(\lambda\mathbb{S})}{\partial\theta}\right)_{p,\lambda\mathcal{M}} = \frac{\lambda\mathbb{C}_V}{\theta} + \left(\frac{\partial\mathbb{S}_{\mathbb{F}^*}}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} \left(\frac{\partial(\lambda\mathbb{V})}{\partial\theta}\right)_{p,\lambda\mathcal{M}} . \tag{3.111}$$

The quantity on the left side is related to the heat capacity at constant pressure according to the definition of Eq. (3.91) so that we obtain

$$\frac{\lambda\mathbb{C}_P}{\theta} = \frac{\lambda\mathbb{C}_V}{\theta} + \left(\frac{\partial\mathbb{S}_{\mathbb{F}^*}}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} \left(\frac{\partial(\lambda\mathbb{V})}{\partial\theta}\right)_{p,\lambda\mathcal{M}} . \tag{3.112}$$

Note that Eq. (3.55) may be differentiated with respect to $\lambda\mathbb{V}$ while holding θ and $\lambda\mathcal{M}$ constant to obtain

$$-\left(\frac{\partial\mathbb{S}_{\mathbb{F}^*}}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} = \left[\frac{\partial}{\partial(\lambda\mathbb{V})}\left(\frac{\partial\mathbb{F}^*}{\partial\theta}\right)_{\lambda\mathbb{V},\lambda\mathcal{M}}\right]_{\theta,\lambda\mathcal{M}} , \tag{3.113}$$

where use has been made of the fact that $\lambda\mathbb{S} = \mathbb{S}_{\mathbb{F}^*}$. Differentiation of Eq. (3.56) with respect to θ while holding $\lambda\mathbb{V}$ and $\lambda\mathcal{M}$ constant provides

$$-\left(\frac{\partial p}{\partial\theta}\right)_{\lambda\mathbb{V},\lambda\mathcal{M}} = \left[\frac{\partial}{\partial\theta}\left(\frac{\partial\mathbb{F}^*}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}}\right]_{\lambda\mathbb{V},\lambda\mathcal{M}} . \tag{3.114}$$

The right sides of these last two equations are equal because the order of differentiation is irrelevant. Therefore, the left sides must also be equal such that[4]

$$\left(\frac{\partial\mathbb{S}_{\mathbb{F}^*}}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} = \left(\frac{\partial p}{\partial\theta}\right)_{\lambda\mathbb{V},\lambda\mathcal{M}} . \tag{3.115}$$

Following substitution of Eq. (3.115) into Eq. (3.112) to eliminate the partial of entropy with respect to volume, we obtain

$$\frac{\lambda\mathbb{C}_P}{\theta} = \frac{\lambda\mathbb{C}_V}{\theta} + \left(\frac{\partial p}{\partial\theta}\right)_{\lambda\mathbb{V},\lambda\mathcal{M}} \left(\frac{\partial(\lambda\mathbb{V})}{\partial\theta}\right)_{p,\lambda\mathcal{M}} . \tag{3.116}$$

The derivative of pressure in Eq. (3.116) can be rearranged directly based on the functional dependence of Eq. (3.60) to show that

$$\left(\frac{\partial p}{\partial\theta}\right)_{\lambda\mathbb{V},\lambda\mathcal{M}} = -\left(\frac{\partial p}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} \left(\frac{\partial(\lambda\mathbb{V})}{\partial\theta}\right)_{p,\lambda\mathcal{M}} . \tag{3.117}$$

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[4] Equalities such as Eq. (3.115), which are obtained by equating second derivatives of energy potentials with respect to two different independent variables, are called Maxwell relations. They are very useful in performing thermodynamic calculations and in replacing quantities that are difficult to control or measure directly (e.g., the left side of Eq. (3.115)) with quantities that are more convenient (e.g., the right side of Eq. (3.115)).

which may be substituted into Eq. (3.116) to obtain

$$\frac{\lambda\mathbb{C}_P}{\theta} = \frac{\lambda\mathbb{C}_V}{\theta} - \left(\frac{\partial p}{\partial(\lambda\mathbb{V})}\right)_{\theta,\lambda\mathcal{M}} \left[\left(\frac{\partial(\lambda\mathbb{V})}{\partial\theta}\right)_{p,\lambda\mathcal{M}}\right]^2 . \tag{3.118}$$

The compressibility under isothermal conditions is denoted as $\hat{\beta}$. It is the relative decrease in volume due to an increase in pressure and is defined as

$$\hat{\beta} = -\frac{1}{\lambda\mathbb{V}}\left(\frac{\partial(\lambda\mathbb{V})}{\partial p}\right)_{\theta,\lambda\mathcal{M}} . \tag{3.119}$$

The thermal expansion coefficient under isobaric conditions is denoted $\hat{\alpha}$ and measures the relative change in volume due to a change in temperature. It is defined as

$$\hat{\alpha} = \frac{1}{\lambda\mathbb{V}}\left(\frac{\partial(\lambda\mathbb{V})}{\partial\theta}\right)_{p,\lambda\mathcal{M}} . \tag{3.120}$$

Substitution of these expressions into Eq. (3.118) provides the simplification

$$\frac{\lambda\mathbb{C}_P}{\theta} = \frac{\lambda\mathbb{C}_V}{\theta} + \lambda\mathbb{V}\frac{\hat{\alpha}^2}{\hat{\beta}} . \tag{3.121}$$

After division by λ and multiplication by θ, we obtain

$$\mathbb{C}_P = \mathbb{C}_V + \theta\mathbb{V}\frac{\hat{\alpha}^2}{\hat{\beta}} . \tag{3.122}$$

This equation makes use of four of the principal parameters that are employed in describing the thermodynamic behavior of fluids, the two heat capacities, the isothermal compressibility, and the coefficient of thermal expansion. The derivation demonstrates that specification of the independent variables being held constant when differentiating a function is essential. In instances when the independent variables associated with a functional specification can be implied unambiguously, such as when using the natural fundamental independent variables with internal energy as in Eq. (3.6), they can be specified implicitly. However, when performing thermodynamic manipulations, it is helpful to make the specifications explicit.

3.7 Solid-phase Equilibrium Thermodynamics

As mentioned in Sect. 3.1, solids behave differently from fluids in that they can sustain a shear stress at equilibrium. Accounting for this property of solids adds additional complications to the specification of the principles of solid thermodynamics. In some instances when the detailed behavior of the solid is not of primary interest, or when the solid deformation only needs to be modeled approximately, the difference between solids and fluids can be effectively accounted for simply by modeling the solid as a highly viscous fluid. If one wishes to follow this approach, the thermodynamic formalism applied for fluids is directly applicable to a solid as well. In a more general approach, a thermodynamic formalism can be proposed that accounts for the fact that in addition to changes in volume, the state of the solid is related to its state of stress. Here we will restrict our attention to elastic solids, a more complex material than a fluid, but a relatively simple solid nonetheless.

An elastic solid is characterized by the fact that its deformation is dependent on the applied stress. When the stress is removed, the elastic solid reverts to its original shape. Also, the history of the deformation is considered to be unimportant, as is the rate at which the deformation occurs, in determining the thermodynamic state of the elastic solid system. The stress that is applied is related to the strain which causes distances between the points in the solid to change. Thus, the thermodynamic formulation for a solid will replace the scalar $\mathbb{V}$ as an independent variable in the postulated form of $\mathbb{E}$ with a tensor that accounts for not only the change in volume but also the change in distances between points in the solid.

To develop the tensor that is needed, we consider a solid phase both before and after a deformation. Let a position vector $\mathbf{X}$ represent a location in the solid phase at some instance prior to deformation. After the deformation has occurred, the point at position $\mathbf{X}$ is considered to have been displaced to a position $\mathbf{x}$. Each point in the system may be displaced so that we can note that the final position of a point depends on its position before the deformation. This situation can be expressed as

$$\mathbf{x} = \mathbf{x}^*(\mathbf{X}) . \tag{3.123}$$

where $\mathbf{x}^*$ is the function that transforms from the initial location to the final location. A point near the position $\mathbf{X}$ is next considered such that its location prior to deformation is $\mathbf{X} + \mathrm{d}\mathbf{X}$. Following the deformation, the location of the point is $\mathbf{x} + \mathrm{d}\mathbf{x}$ such that

$$\mathbf{x} + \mathrm{d}\mathbf{x} = \mathbf{x}^*(\mathbf{X} + \mathrm{d}\mathbf{X}) . \tag{3.124}$$

Combination of Eqs. (3.123) and (3.124) to eliminate $\mathbf{x}$ yields

$$\mathrm{d}\mathbf{x} = \mathbf{x}^*(\mathbf{X} + \mathrm{d}\mathbf{X}) - \mathbf{x}^*(\mathbf{X}) . \tag{3.125}$$

If we make a Taylor series expansion around the initial location we obtain

$$\mathbf{x}^*(\mathbf{X} + \mathrm{d}\mathbf{X}) = \mathbf{x}^*(\mathbf{X}) + \left.(\nabla_X \mathbf{x}^*)^{\mathrm{T}}\right|_{\mathbf{X}} \cdot \mathrm{d}\mathbf{X} + \ldots , \tag{3.126}$$

where the higher order terms in the expansion are not listed because they are considered negligible. The indicated dot product is between $\mathrm{d}\mathbf{X}$ and the gradient operator with respect to $\mathbf{X}$ coordinates. Substitution of Eq. (3.126) into Eq. (3.125) then gives

$$\mathrm{d}\mathbf{x} = \left.(\nabla_X \mathbf{x}^*)^{\mathrm{T}}\right|_{\mathbf{X}} \cdot \mathrm{d}\mathbf{X} . \tag{3.127}$$

The square of the change in length between two points is

$$\mathrm{d}x^2 = \mathrm{d}\mathbf{x}\cdot\mathrm{d}\mathbf{x}\,. \tag{3.128}$$

Substitution of Eq. (3.127) into the right side of this equation yields

$$\mathrm{d}x^2 = \left[\nabla_X \mathbf{x}^* \cdot (\nabla_X \mathbf{x}^*)^{\mathrm{T}}\right]\Big|_{\mathbf{X}} : \mathrm{d}\mathbf{X}\,\mathrm{d}\mathbf{X}\,. \tag{3.129}$$

The measure of strain known as the Green's deformation tensor, or the right Cauchy-Green deformation tensor, C, is defined as

$$\mathsf{C} = \nabla_X \mathbf{x}^* \cdot (\nabla_X \mathbf{x}^*)^{\mathrm{T}}\ , \tag{3.130}$$

and it is more conveniently written as

$$\mathsf{C} = \nabla_X \mathbf{x} \cdot (\nabla_X \mathbf{x})^{\mathrm{T}}\ , \tag{3.131}$$

making use of Eq. (3.123).

With this measure of strain, which incidentally is not the only measure of strain possible [e.g., 6, 13, discuss other measures of strain such as the Lagrangian and Eulerian strain tensor and the left Cauchy-Green deformation tensor], we have a quantity that can be used both to indicate the deformation of the solid and its dilatation (change in volume) from an initial configuration. Recall that the initial postulate of the form of internal energy for a fluid was in terms of extensive variables. The Green's deformation tensor is an intensive variable as its value will be unchanged when two identical systems are combined. However, an extensive variable can be constructed by multiplying C by the initial volume of the solid, $\mathbb{V}_0$. Thus the tensor $\mathbb{V}_0\mathsf{C}$ will replace $\mathbb{V}$ in the postulated form of the solid-phase internal energy. With reference to Eq. (3.16), the solid-phase internal energy is postulated to be described as

$$\lambda\mathbb{E} = \mathbb{E}^*(\lambda\mathbb{S}, \lambda\mathbb{V}_0\mathsf{C}, \lambda\mathcal{M})\,. \tag{3.132}$$

This form for the solid-phase internal energy replaces the single variable, $\mathbb{V}$, employed when describing a fluid with the six different unique components of the symmetric tensor, C, multiplied by the initial system volume, $\mathbb{V}_0$.

Differentiation of Eq. (3.132) gives the equation similar to Eq. (3.18)

$$\begin{aligned}\mathrm{d}(\lambda\mathbb{E}) = {} & \left(\frac{\partial\mathbb{E}^*}{\partial(\lambda\mathbb{S})}\right)_{\lambda\mathbb{V}_0\mathsf{C},\lambda\mathcal{M}} \mathrm{d}(\lambda\mathbb{S}) + \left(\frac{\partial\mathbb{E}^*}{\partial(\lambda\mathbb{V}_0\mathsf{C})}\right)_{\lambda\mathbb{S},\lambda\mathcal{M}} : \mathrm{d}(\lambda\mathbb{V}_0\mathsf{C}) \\ & + \sum_{i\in\mathcal{I}_s} \left(\frac{\partial\mathbb{E}^*}{\partial(\lambda\mathbb{M}_i)}\right)_{\lambda\mathbb{S},\lambda\mathbb{V}_0\mathsf{C},\lambda\mathcal{M}_i} \mathrm{d}(\lambda\mathbb{M}_i)\ .\end{aligned} \tag{3.133}$$

All quantities multiplied by λ are extensive quantities. Here, as with the exposition of the fluid phase, we have included the parameter λ in anticipation of looking at the formulation in terms of extensive variables, by selection of $\lambda = 1$, or in terms of energy per volume or mass depending on the value selected for λ. For the solid, temperature, the symmetric stress tensor[5], and chemical potential are defined, respectively, as

$$\theta = \left(\frac{\partial \mathbb{E}^*}{\partial(\lambda\mathbb{S})}\right)_{\lambda\mathbb{V}_0\mathbf{C},\lambda\mathcal{M}} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{S}} \ , \tag{3.134}$$

$$\boldsymbol{\sigma} = \left(\frac{\partial \mathbb{E}^*}{\partial(\lambda\mathbb{V}_0\mathbf{C})}\right)_{\lambda\mathbb{S},\lambda\mathcal{M}} \qquad \text{for } \lambda \not\propto (\mathbf{C}^{-1})_{ij} \ , \tag{3.135}$$

and

$$\mu_i = \left(\frac{\partial \mathbb{E}^*}{\partial(\lambda\mathbb{M}_i)}\right)_{\lambda\mathbb{S},\lambda\mathbb{V}_0\mathbf{C},\lambda\mathcal{M}_i} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{M}_i} \ , \tag{3.136}$$

where the value of λ is arbitrary. The constraint on λ indicated in Eq. (3.135) is necessary for specification of the (i,j) member of $\boldsymbol{\sigma}$. With these definitions employed in Eq. (3.133), we obtain the differential of the internal energy of the solid as

$$\mathrm{d}(\lambda\mathbb{E}) = \theta\,\mathrm{d}(\lambda\mathbb{S}) + \boldsymbol{\sigma}{:}\mathrm{d}(\lambda\mathbb{V}_0\mathbf{C}) + \sum_{i\in\mathfrak{I}_s} \mu_i\,\mathrm{d}(\lambda\mathbb{M}_i) \ . \tag{3.137}$$

The equations of state for the intensive thermodynamic parameters for the solid are written as

$$\theta = \theta_{\mathbb{E}^*}(\lambda\mathbb{S},\lambda\mathbb{V}_0\mathbf{C},\lambda\mathcal{M}) \ , \tag{3.138}$$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\mathbb{E}^*}(\lambda\mathbb{S},\lambda\mathbb{V}_0\mathbf{C},\lambda\mathcal{M}) \ , \tag{3.139}$$

and

$$\mu_i = \mu_{\mathbb{E}^*i}(\lambda\mathbb{S},\lambda\mathbb{V}_0\mathbf{C},\lambda\mathcal{M}) \ . \tag{3.140}$$

These equations of state are homogeneous zero-order equations. When scaling the size of the homogeneous system, the values of the intensive thermodynamic variables are not affected.

Subsequent manipulations with the solid-phase thermodynamic equations are analogous to those employed when considering fluid phases. Because Eq. (3.132) is first order homogeneous, it follows directly, in conjunction with Eq. (3.137), that the Euler form for internal energy of a solid analogous to Eq. (3.34) is

$$\lambda\mathbb{E} = \theta\lambda\mathbb{S} + \boldsymbol{\sigma}{:}\lambda\mathbb{V}_0\mathbf{C} + \sum_{i\in\mathfrak{I}_s} \mu_i\lambda\mathbb{M}_i \ . \tag{3.141}$$

With $\lambda = 1$, the Euler equation is expressed for the full system. Selection of $\lambda = 1/\mathbb{V}$ yields

$$E = \theta\eta + \boldsymbol{\sigma}{:}\frac{\mathbf{C}}{j} + \sum_{i\in\mathfrak{I}_s} \mu_i\rho\omega_i \ , \tag{3.142}$$

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[5] The quantity $\boldsymbol{\sigma}$ is equal to one half the classical second Piola-Kirchhoff stress tensor [21], one of many measures of stress that are encountered in solid mechanics.

where j is the jacobian, the ratio of the volume of the system after deformation to its volume before deformation, $j = \mathbb{V}/\mathbb{V}_0$. The corresponding Gibbs-Duhem equation is

$$0 = \eta\,\mathrm{d}\theta + \frac{\mathsf{C}}{j}{:}\mathrm{d}\boldsymbol{\sigma} + \sum_{i\in\mathfrak{I}_s} \rho\omega_i\,\mathrm{d}\mu_i\,. \tag{3.143}$$

Transformation from internal energy to other energy potentials is accomplished for solids in a manner similar to that employed for fluids. Thus, these manipulations are not supplied here but are encouraged in the exercises at the end of the chapter.

In summary, the mechanics and thermodynamics of solids is a complex field because of the different behaviors that solids can exhibit when subjected to stress. The formulation presented here is for anisotropic elastic solids. We do not account for solid fatigue, fracturing, or plasticity. The presentation here is abbreviated and is intended simply to provide enough information on the equilibrium thermodynamics of elastic solids to support their incorporation into models of porous medium flow. Those interested in more comprehensive introductions to and knowledge of the behavior of solids and the description of that behavior are referred to the literature [e.g., 1, 2, 5, 13, 44]. However, it is useful to understand that the mathematical description of solid properties is usually developed in the context of mechanics, with a thermodynamic approach in the context of postulation of energy dependences being employed less frequently.

3.8 Interface and Common Curve Equilibrium Thermodynamics

Because the TCAT models of concern involve not only phases but also interfaces that exist between two phases and common curves that form at the boundary of three phases, thermodynamic expressions are needed for these entities. Interfaces and common curves are, in fact, idealized entities that account for the change in properties of a phase in the vicinity of other phases because of molecular interaction forces between phases. The manifestation of these forces is well known in basic physical analysis, and significant progress has been made in incorporating these phenomena into thermodynamic theory [7, 16, 17, 41, 48, 57].

At the molecular scale, the change in molecular orientation and inter-molecular potential varies in space. For a two-fluid-phase system the region of largest change often occurs as one approaches the transition between phases. This same behavior exists at larger scales. One way to account for such sharp gradients in material properties is to introduce interface entities, which can have mass, momentum, energy, entropy, and thermodynamic properties. This approach is reasonable when the length scale of the transition is much less than the length scale of the phases on each side of the transition region. This approach will be adopted here, where we will consider interfaces to be two-dimensional regions that separate phases and consider common curves to be one-dimensional regions that form where interfaces that separate three pairs of phases come together.

Although interfaces and common curves provide additional thermodynamic properties to those of phases, their impact on many systems can be neglected. For example, if the curvature of an interface or common curve multiplied by the characteristic length of a phase is much less than 1, contributions of these regions to the system thermodynamic behavior will be negligible. For multiphase porous medium systems where the diameter of a pore, which is roughly the characteristic length of the fluid phase, is often of the same order of magnitude as the radius of curvature of the interface or common curve, the interfaces and curves can play prominent roles in determining the system behavior. Thus, it will be important to account for the mechanics and thermodynamics of these entities in a general TCAT model.

To develop the thermodynamic description of interfaces and common curves, a similar approach is employed to that used for phases. The internal energy is postulated to be a function of extensive variables such that the Euler equation obtained is first order homogeneous. After that has been accomplished, the manipulations to obtain the definitions of the intensive variables, equations of state, and the Gibbs-Duhem equation follow analogously.

3.8.1 Interface Thermodynamics

The most important task in describing the equilibrium thermodynamics of an interface is the selection of the independent variables on which the internal energy depends. We first hypothesize that this dependence will be a variant of Eq. (3.32) for a phase that occupies volume by replacing $\mathbb{V}$ with $\mathbb{A}$, the area of the interface. Additionally, it seems reasonable that the energy might depend on the curvature of the interface. However, since extensive independent variables are sought, it may be appropriate to multiply these curvatures by the interfacial area. Thus, the independent variables will all be extensive quantities. From these thoughts, the internal energy for a surface is postulated to have the functional dependence

$$\lambda\mathbb{E} = \mathbb{E}^*(\lambda\mathbb{S}, \lambda\mathbb{A}, \lambda\mathcal{M}, J\lambda\mathbb{A}, K\lambda\mathbb{A}) , \tag{3.144}$$

where J is the first curvature (equal to the sum of the principal curvatures) and K is the second, or Gaussian, curvature (equal to the product of the principal curvatures) [3, 4]. The first and second curvatures, derived from the principal curvatures, are selected for this expression rather than the principal curvatures themselves because they are invariants of the surface.

For the case of a spherical interface, $J^2 = 4K$ such that only one of the curvatures must be specified. For flat interfaces, both J and K equal zero. In this instance the interfacial curvatures are not included in the formulation. Indeed, we will adopt the convention here, for simplicity rather than necessity, that the curvatures of the interface do not become large enough in the systems we will model that they need to be included in the postulation of thermodynamic dependence. Although this convention restricts the thermodynamic formulation, it has been found experimentally to be a good approximation for many systems. The influence of curvature on surface thermodynamic properties is rarely included. Thus the expression for the interfacial thermodynamics is

$$\lambda\mathbb{E} = \mathbb{E}^*(\lambda\mathbb{S}, \lambda\mathbb{A}, \lambda\mathcal{M}) \; . \tag{3.145}$$

With this form, Eqs. (3.16)–(3.24) are reproduced with $\mathbb{A}$ replacing $\mathbb{V}$ as an extensive independent variable and γ, the surface tension, replacing $-p$ in the definitions and resulting equations with

$$\gamma = \left(\frac{\partial\mathbb{E}^*}{\partial(\lambda\mathbb{A})}\right)_{\lambda\mathbb{S},\lambda\mathcal{M}} \qquad \text{for } \lambda \not\propto \frac{1}{\mathbb{A}} \; . \tag{3.146}$$

The derivation will not be presented explicitly. However, the Euler equation obtained is

$$\lambda\mathbb{E} = \theta\lambda\mathbb{S} + \gamma\lambda\mathbb{A} + \sum_{i\in\mathfrak{I}_s} \mu_i\lambda\mathbb{M}_i \; ; \tag{3.147}$$

its differential is

$$\mathrm{d}(\lambda\mathbb{E}) = \theta\,\mathrm{d}(\lambda\mathbb{S}) + \gamma\,\mathrm{d}(\lambda\mathbb{A}) + \sum_{i\in\mathfrak{I}_s} \mu_i\,\mathrm{d}(\lambda\mathbb{M}_i) \; ; \tag{3.148}$$

and the corresponding Gibbs-Duhem equation is obtained as

$$0 = \lambda\mathbb{S}\,\mathrm{d}\theta + \lambda\mathbb{A}\,\mathrm{d}\gamma + \sum_{i\in\mathfrak{I}_s} \lambda\mathbb{M}_i\,\mathrm{d}\mu_i \; . \tag{3.149}$$

Selection of $\lambda = 1$ in the preceding equations gives the forms of the Euler and Gibbs-Duhem equations in terms of extensive variables. Rather than selecting $\lambda = 1/\mathbb{V}$ as was done for the phases to obtain equations in terms of densities, we select $\lambda = 1/\mathbb{A}$ to obtain densities for surfaces as quantities per unit area. Thus, for example, Eq. (3.147) will be

$$E = \theta\eta + \gamma + \sum_{i\in\mathfrak{I}_s} \mu_i\rho\omega_i \; , \tag{3.150}$$

where E is internal energy per area, η is entropy per area, and ρ is mass per area.

When working with phases, it is common to re-express extensive variables on a per unit mass basis by selecting $\lambda = 1/\mathbb{M}$. A similar approach could be adopted with surfaces, but it has a serious pitfall. In many instances, it will be convenient to model surfaces as being massless. In those cases, surface properties per unit mass of surface are ill-defined. For this reason, when employing thermodynamic relations, we will work with density forms with variables defined per unit measure of the extent of the entity (e.g., volume, area, length, or number).

3.8.2 Common Curve Thermodynamics

For curves, the selection of independent variables is somewhat more complex than for surfaces. The normal curvature, geodesic curvature, and geodesic torsion, all properties inherent to the curve, could impact its thermodynamic state. Additionally, one might hypothesize that the angles between the surfaces that meet at the common curve would impact the common curve state. Alternative ways to incorporate these variables have been proposed [4, 57]. Here we will adopt an approach similar to that employed with surfaces and presume that the amount of distortion of the curve from a straight line and the angles between the interface that meet to form the curve have negligible impact on its thermodynamic state. Again, this is not a necessary assumption but is reasonable for many systems and allows for simplification.

With these considerations, the functional dependence presumed for the common curve is

$$\lambda\mathbb{E} = \mathbb{E}^*(\lambda\mathbb{S}, \lambda\mathbb{L}, \lambda\mathcal{M}) , \tag{3.151}$$

where $\mathbb{L}$ is the extent of the common curve, its length. Therefore the expression for the derivative, the definitions of the intensive variables and the equations of state analogous to Eqs. (3.16)–(3.24) are obtained with $\mathbb{L}$ replacing $\mathbb{V}$ as an extensive independent variable and γ, the lineal tension, replacing p. The lineal tension is defined as

$$-\gamma = \left(\frac{\partial\mathbb{E}^*}{\partial(\lambda\mathbb{L})}\right)_{\lambda\mathbb{S},\lambda\mathcal{M}} \qquad \text{for } \lambda \not\ll \frac{1}{\mathbb{L}} . \tag{3.152}$$

Note that the symbol γ is used for both lineal and interfacial tension, but with different signs in their definition. Interfacial tension behaves such that it is positive, i.e., the interfacial energy increases as a surface is stretched. The lineal tension, on the other hand, can be negative or positive depending on the behavior of the curve with some curves being resistant to stretching, such that their lineal tension is negative as defined here, while other curves are resistant to compression, such that their lineal tension is positive. Of course, the introduction of the minus sign in the definition of γ for a curve is an arbitrary selection. The main point is that pressure and surface tension are defined such that they are always positive while the sign of lineal tension is material dependent.

For a common curve, the Euler equation for internal energy is

$$\lambda\mathbb{E} = \theta\lambda\mathbb{S} - \gamma\lambda\mathbb{L} + \sum_{i\in\mathcal{I}_s} \mu_i\lambda\mathbb{M}_i , \tag{3.153}$$

and the corresponding Gibbs-Duhem equation is obtained as

$$0 = \lambda\mathbb{S}\,\mathrm{d}\theta - \lambda\mathbb{L}\,\mathrm{d}\gamma + \sum_{i\in\mathcal{I}_s} \lambda\mathbb{M}_i\,\mathrm{d}\mu_i . \tag{3.154}$$

The Euler and Gibbs-Duhem equations for a common curve are thus obtained in terms of extensive variables when $\lambda = 1$. Because the domain of the curve is one-dimensional, the densities of the extensive variables are quantities per length of curve. Thus selection of $\lambda = 1/\mathbb{L}$ expresses Eq. (3.153) as

$$E = \theta\eta - \gamma + \sum_{i\in\mathfrak{I}_s} \mu_i \rho \omega_i \, , \tag{3.155}$$

where E is internal energy per length, η is entropy per length, and ρ is mass per length.

With common curves, as with interfaces, the selection of $\lambda = \mathbb{M}$ is allowable. However, this choice can restrict the applicability of the resultant form, since modeling of massless common curves in terms of quantities per unit mass provides an inherent contradiction. Thus, at the microscale, densities expressed per unit length are more widely applicable.

3.9 Microscale Multiphase System Notation

The equilibrium thermodynamic framework detailed to this point has not employed notation that points particularly to one phase, interface, or common curve. Because, in general, we will be concerned with systems that involve multiple phases, a need exists to supplement the notation employed to distinguish among entities. For microscale quantities, as discussed in this chapter, we will use subscripts to designate the various entities, following the same approach as in Chap. 2. For example, the Euler equation describing the internal energy density function of a fluid, Eq. (3.42), can be written as

$$E_\alpha = \theta_\alpha \eta_\alpha - p_\alpha + \sum_{i\in\mathfrak{I}_s} \mu_{i\alpha} \rho_\alpha \omega_{i\alpha} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{f} \, ; \tag{3.156}$$

and the corresponding microscale Gibbs-Duhem equation, Eq. (3.43), is

$$0 = \eta_\alpha \, \mathrm{d}\theta_\alpha - \mathrm{d}p_\alpha + \sum_{i\in\mathfrak{I}_s} \rho_\alpha \omega_{i\alpha} \, \mathrm{d}\mu_{i\alpha}, \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{f} \, , \tag{3.157}$$

where α identifies the phase and $\mathfrak{I}_\mathrm{f}$ is the index set of fluid phases. For a system composed of three fluid phases, two liquids and a gas, along with a solid phase, we will denote the liquid phase that preferentially wets the solid as w, the non-wetting phase as n, and the gas phase as g. Therefore, in this instance, $\mathfrak{I}_\mathrm{f} = \{w, n, g\}$, and the Euler form for the wetting phase is written

$$E_w = \theta_w \eta_w - p_w + \sum_{i\in\mathfrak{I}_s} \mu_{iw} \rho_w \omega_{iw} \, . \tag{3.158}$$

Note that in some physical systems where the surface properties of the solid are not uniform, a phase may be wetting in one region and non-wetting in a different region of space. Thus, the subscript designations might be selected differently to distinguish among fluid phases. Here, we will not explicitly concern ourselves with this notational issue.

In the derivations in this text, we will examine porous medium systems that have a single solid phase along with the fluid phases. A subscript s will be used to identify a microscale property of the solid. For example, the subscripted form of the internal energy Euler equation for a solid, Eq. (3.142), is

$$E_s = \theta_s \eta_s + \boldsymbol{\sigma}_s : \frac{\mathsf{C}_s}{j_s} + \sum_{i \in \mathfrak{I}_s} \mu_{is} \rho_s \omega_{is} \ . \tag{3.159}$$

The corresponding Gibbs-Duhem equation, based on Eq. (3.143), is

$$0 = \eta_s \, \mathrm{d}\theta_s + \frac{\mathsf{C}_s}{j_s} : \mathrm{d}\boldsymbol{\sigma}_s + \sum_{i \in \mathfrak{I}_s} \rho_s \omega_{is} \, \mathrm{d}\mu_{is} \ . \tag{3.160}$$

In multiphase systems, the thermodynamic properties of the interfaces between phases and of the common curves must be accounted for. A subscript notation is employed to account for these entities. For example, if a system is composed of w, n, and s phases, three different types of interfaces can be identified, depending on which phases they separate. These are designated as the wn, ws, and ns interfaces where the two letters designate the adjacent phases. The order of the indices is not important (e.g., a wn interface is equivalent to an nw interface), but we will make use only of one option. With this convention, the Euler equation for an interface given by Eq. (3.147) can be expressed

$$E_\alpha = \theta_\alpha \eta_\alpha + \gamma_\alpha + \sum_{i \in \mathfrak{I}_s} \mu_{i\alpha} \rho_\alpha \omega_{i\alpha} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{I}} \ , \tag{3.161}$$

where $\mathfrak{I}_{\mathrm{I}}$ is the set of interface indices such that $\mathfrak{I}_{\mathrm{I}} = \{wn, ws, ns\}$. If a particular interface is of interest, such as the one between the w and n phases, the Euler equation for this interface can be written as

$$E_{wn} = \theta_{wn} \eta_{wn} + \gamma_{wn} + \sum_{i \in \mathfrak{I}_s} \mu_{iwn} \rho_{wn} \omega_{iwn} \ . \tag{3.162}$$

The convention for using subscripts to identify microscale properties is extended to apply to common curve thermodynamics as well. Thus, for example, the Euler equation for the internal energy of a common curve follows directly from Eq. (3.153) as

$$E_\alpha = \theta_\alpha \eta_\alpha - \gamma_\alpha + \sum_{i \in \mathfrak{I}_s} \mu_{i\alpha} \rho_\alpha \omega_{i\alpha} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{C}} \ , \tag{3.163}$$

where $\mathfrak{I}_{\mathrm{C}}$ is the set of common curve indices. For a three-phase system composed of w, n, and s phases, $\mathfrak{I}_{\mathrm{C}} = \{wns\}$ and the order of indices is inconsequential. If a gas phase, g, is added to the three phases, then $\mathfrak{I}_{\mathrm{C}} = \{wns, wng, wsg, nsg\}$ because four different types of common curves can be formed. The Euler equation for the wns common curve can be written specifically as

$$E_{wns} = \theta_{wns}\eta_{wns} - \gamma_{wns} + \sum_{i\in\mathfrak{I}_s} \mu_{iwns}\rho_{wns}\omega_{iwns} \,. \tag{3.164}$$

The apparent digression here regarding notation is made because keeping the notation straight so that systems, phases, interfaces, and common curves are clearly denoted along with their scales is absolutely crucial to the TCAT formulation. This can lead to some rather daunting looking expressions. However, if the meaning of the notation is kept in mind, it will not be a serious obstacle to understanding what is being denoted and modeled.

3.10 Partial Mass Quantities

The definitions of the energy for fluids, solids, interfaces, and common curves as given in Eqs. (3.28), (3.141), (3.147), and (3.153), respectively, apply to entities as a whole. In some instances, it will be useful to have measures of thermodynamic variables that are properties of species within the entity. Such a quantity has already been employed in denoting $\mu_{i\alpha}$ as the chemical potential of species i in entity α. Thermodynamic relations for species are employed here using partial mass quantities, which are particular derivatives of extensive thermodynamic properties of an entity with respect to the mass of a species of interest while holding temperature, the masses of all other species, and an appropriate measure of stress constant.[6] Partial mass quantities express how an extensive thermodynamic property changes with the mass of one of the species while the designated variables are held constant. For convenience, partial mass quantities for the various entities of interest are defined in the following subsections.

3.10.1 Fluid Phase

We begin with Eq. (3.28), subscripted to designate that this is the microscale expression for the internal energy of fluid phase α composed of the species in the set $\mathfrak{I}_s$,

$$\mathbb{E}_\alpha = \theta_\alpha \mathbb{S}_\alpha - p_\alpha \mathbb{V}_\alpha + \sum_{k\in\mathfrak{I}_s} \mu_{k\alpha}\mathbb{M}_{k\alpha} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{f} \,. \tag{3.165}$$

Recall the set $\mathcal{M}_i$ defined in Eq. (3.4) which consists of all species in the entity except for species i. This set may be used to refer to species in entity α with the notation $\mathcal{M}_{i\alpha}$. Thus the differential of Eq. (3.165) with respect to $\mathbb{M}_{i\alpha}$ while holding

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[6] Typically, partial molar quantities are employed. These are obtained by differentiating the extensive thermodynamic quantities with respect to the number of moles of a chemical species. Thus, partial mass and partial molar properties may be interchanged by multiplying by the molecular weight of the species. For our purposes, the partial mass forms are more easily directly integrated into our equations.

p_α, θ_α, and the masses of all species except i constant is

$$\left(\frac{\partial \mathbb{E}_\alpha}{\partial \mathbb{M}_{i\alpha}}\right)_{p_\alpha,\theta_\alpha,\mathcal{M}_{i\alpha}} = \theta_\alpha \left(\frac{\partial \mathbb{S}_\alpha}{\partial \mathbb{M}_{i\alpha}}\right)_{p_\alpha,\theta_\alpha,\mathcal{M}_{i\alpha}} - p_\alpha \left(\frac{\partial \mathbb{V}_\alpha}{\partial \mathbb{M}_{i\alpha}}\right)_{p_\alpha,\theta_\alpha,\mathcal{M}_{i\alpha}} + \mu_{i\alpha} \, . \tag{3.166}$$

By definition, the partial derivatives in this expression are partial mass quantities denoted using overbars, so that Eq. (3.166) may be written as

$$\overline{E}_{i\alpha} = \theta_\alpha \overline{\eta}_{i\alpha} - p_\alpha \overline{V}_{i\alpha} + \mu_{i\alpha} \, , \tag{3.167}$$

where, for example,

$$\overline{E}_{i\alpha} = \left(\frac{\partial \mathbb{E}_\alpha}{\partial \mathbb{M}_{i\alpha}}\right)_{p_\alpha,\theta_\alpha,\mathcal{M}_{i\alpha}} \, . \tag{3.168}$$

The partial mass quantities are properties per unit mass of species i. They can be converted to quantities per unit volume of fluid entity α by multiplying them by $\rho_\alpha \omega_{i\alpha}$ so that Eq. (3.167) becomes

$$E_{i\alpha} = \theta_\alpha \eta_{i\alpha} - p_\alpha X_{i\alpha} + \rho_\alpha \omega_{i\alpha} \mu_{i\alpha} \quad \text{for } \alpha \in \mathcal{J}_\mathrm{f} \, , \tag{3.169}$$

where

$$E_{i\alpha} = \rho_\alpha \omega_{i\alpha} \overline{E}_{i\alpha} \, , \tag{3.170}$$

$$\eta_{i\alpha} = \rho_\alpha \omega_{i\alpha} \overline{\eta}_{i\alpha} \, , \tag{3.171}$$

and

$$X_{i\alpha} = \rho_\alpha \omega_{i\alpha} \overline{V}_{i\alpha} \, . \tag{3.172}$$

The sums of $E_{i\alpha}$ and of $\eta_{i\alpha}$ over all species i yield E_α and η_α, respectively. Additionally, the sum of $X_{i\alpha}$ over all species i is equal to 1. Thus, the sum of Eq. (3.169) over all species provides the Euler equation for the energy per volume of a fluid entity as given in Eq. (3.156).

After all terms have been moved to the left side of the equation, the differential of Eq. (3.169) is

$$\mathrm{d}E_{i\alpha} - \theta_\alpha \mathrm{d}\eta_{i\alpha} + p_\alpha \mathrm{d}X_{i\alpha} - \mu_{i\alpha} \mathrm{d}\left(\rho_\alpha \omega_{i\alpha}\right) - \rho_\alpha \omega_{i\alpha} \left.\left(\mathrm{d}\mu_{i\alpha}\right)\right|_{p_\alpha,\theta_\alpha} = 0$$

$$\text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_\mathrm{f} \, , \tag{3.173}$$

where the vertical bar with the subscripts indicates the differential of $\mu_{i\alpha}$ is taken while holding p_α and θ_α constant such that

$$\left.\left(\mathrm{d}\mu_{i\alpha}\right)\right|_{p_\alpha,\theta_\alpha} = \sum_{k \in \mathcal{J}_s} \left(\frac{\partial \mu_{i\alpha}}{\partial \mathbb{M}_{k\alpha}}\right)_{p_\alpha,\theta_\alpha,\mathcal{M}_{i\alpha}} \mathrm{d}\mathbb{M}_{k\alpha} \, . \tag{3.174}$$

Thus, the species-based Gibbs-Duhem equation is

$$\rho_\alpha\omega_{i\alpha}\mathrm{d}\mu_{i\alpha}+\eta_{i\alpha}\mathrm{d}\theta_\alpha-X_{i\alpha}\mathrm{d}p_\alpha-\rho_\alpha\omega_{i\alpha}\left.(\mathrm{d}\mu_{i\alpha})\right|_{p_\alpha,\theta_\alpha}=0\quad\text{for } i\in\mathcal{I}_s,\alpha\in\mathcal{I}_\mathrm{f}\,. \tag{3.175}$$

We comment that the relations among thermodynamic potentials introduced in Sect. 3.5 are preserved when written in terms of partial mass quantities. For example, we can begin with Eq. (3.78) with λ selected to equal 1. We then append the subscript to designate an entity, α. Differentiation with respect to $\mathbb{M}_{k\alpha}$ while holding p_α, θ_α, and the masses of all species except k constant gives

$$\left(\frac{\partial\mathbb{H}_\alpha}{\partial\mathbb{M}_{k\alpha}}\right)_{p_\alpha,\theta_\alpha,\mathcal{M}_{k\alpha}}=\theta_\alpha\left(\frac{\partial\mathbb{S}_\alpha}{\partial\mathbb{M}_{k\alpha}}\right)_{p_\alpha,\theta_\alpha,\mathcal{M}_{k\alpha}}+\mu_{k\alpha}\,, \tag{3.176}$$

or

$$\overline{H}_{k\alpha}=\theta_\alpha\overline{\eta}_{k\alpha}+\mu_{k\alpha}\,. \tag{3.177}$$

Multiplication by $\rho_\alpha\omega_{k\alpha}$ provides

$$H_{k\alpha}=\theta_\alpha\eta_{k\alpha}+\rho_\alpha\omega_{k\alpha}\mu_{k\alpha}\quad\text{for } k\in\mathcal{I}_s,\alpha\in\mathcal{I}\,. \tag{3.178}$$

3.10.2 Solid Phase

Development of the partial mass expressions for a solid phase is similar to that for a fluid phase but takes into account the dependence of energy on $\mathbb{V}_{0s}\mathbf{C}_s$ rather than on just the volume, $\mathbb{V}_s$. The Euler equation for an elastic solid is Eq. (3.141) modified by selecting $\lambda=1$ and by adding the subscript s to refer to the solid-phase properties. Thus we begin with

$$\mathbb{E}_s=\theta_s\mathbb{S}_s+\boldsymbol{\sigma}_s{:}\mathbb{V}_{0s}\mathbf{C}_s+\sum_{k\in\mathcal{I}_s}\mu_{ks}\mathbb{M}_{ks}\,. \tag{3.179}$$

The differential of this equation taken with respect to $\mathbb{M}_{is}$ while holding $\boldsymbol{\sigma}_s$, θ_s, and all species masses other than i, $\mathcal{M}_{is}$, constant yields

$$\left(\frac{\partial\mathbb{E}_s}{\partial\mathbb{M}_{is}}\right)_{\boldsymbol{\sigma}_s,\theta_s,\mathcal{M}_{is}}=\theta_s\left(\frac{\partial\mathbb{S}_s}{\partial\mathbb{M}_{is}}\right)_{\boldsymbol{\sigma}_s,\theta_s,\mathcal{M}_{is}}+\boldsymbol{\sigma}_s{:}\left(\frac{\partial(\mathbb{V}_{0s}\mathbf{C}_s)}{\partial\mathbb{M}_{is}}\right)_{\boldsymbol{\sigma}_s,\theta_s,\mathcal{M}_{is}}+\mu_{is}\,. \tag{3.180}$$

The partial derivatives in this expression are partial mass quantities. Therefore Eq. (3.180) may be written

$$\overline{E}_{is}=\theta_s\overline{\eta}_{is}+\boldsymbol{\sigma}_s{:}\frac{\overline{\mathbf{C}}_{is}}{j_s}+\mu_{is}\,. \tag{3.181}$$

Multiplication by $\rho_s\omega_{is}$ to change the partial mass quantities to a per-unit-volume basis yields

$$E_{is} = \theta_s \eta_{is} + \boldsymbol{\sigma}_s : \frac{\mathbf{X}_{is} \cdot \mathbf{C}_s}{j_s} + \rho_s \omega_{is} \mu_{is} \,, \tag{3.182}$$

where

$$E_{is} = \rho_s \omega_{is} \overline{E}_{is} \,, \tag{3.183}$$

$$\eta_{is} = \rho_s \omega_{is} \overline{\eta}_{is} \,, \tag{3.184}$$

and

$$\mathbf{X}_{is} = \rho_s \omega_{is} \overline{\mathbf{C}}_{is} \cdot \mathbf{C}_s^{-1} \,, \tag{3.185}$$

with

$$\mathbf{I} = \sum_{i \in \mathfrak{J}_s} \mathbf{X}_{is} \,. \tag{3.186}$$

After all terms have been moved to the left side, the differential of Eq. (3.182) is

$$\mathrm{d}E_{is} - \theta_s \mathrm{d}\eta_{is} - \boldsymbol{\sigma}_s : \mathrm{d}\left(\frac{\mathbf{X}_{is} \cdot \mathbf{C}_s}{j_s} \right) - \mu_{is} \mathrm{d}\left(\rho_s \omega_{is}\right) - \rho_s \omega_{is} \left(\mathrm{d}\mu_{is}\right)\big|_{\boldsymbol{\sigma}_s, \theta_s} = 0 \quad \text{for } i \in \mathfrak{J}_s \,. \tag{3.187}$$

The species-based Gibbs-Duhem equation in the solid phase is

$$\rho_s \omega_{is} \mathrm{d}\mu_{is} + \eta_{is} \mathrm{d}\theta_s + \frac{\mathbf{X}_{is} \cdot \mathbf{C}_s}{j_s} : \mathrm{d}\boldsymbol{\sigma}_s - \rho_s \omega_{is} \left(\mathrm{d}\mu_{is}\right)\big|_{\boldsymbol{\sigma}_s, \theta_s} = 0 \quad \text{for } i \in \mathfrak{J}_s \,. \tag{3.188}$$

3.10.3 Interface

The derivation of partial mass quantities for an interface is analogous to the derivation for the fluid phases with pressure replaced by negative interfacial tension and volume replaced by area. The starting point is Eq. (3.147) with subscripts added to indicate the surface being considered. Because the development of the differentials of the species differential of energy and of the species Gibbs-Duhem equation follows Eqs. (3.165)–(3.175) so closely, only the results for the interface will be provided here.

Based on the partial mass Euler equation, we obtain

$$E_{i\alpha} = \theta_\alpha \eta_{i\alpha} + \gamma_\alpha X_{i\alpha} + \rho_\alpha \omega_{i\alpha} \mu_{i\alpha} \quad \text{for } \alpha \in \mathfrak{J}_\mathrm{I} \,, \tag{3.189}$$

where

$$X_{i\alpha} = \rho_\alpha \omega_{i\alpha} \overline{A}_{i\alpha} \tag{3.190}$$

and the other quantities are defined as in Eqs. (3.170)–(3.171). Remember that the energy, entropy, and mass densities in Eq. (3.189) are all per unit area of interface. The sum of Eq. (3.189) over all species gives the Euler equation for energy per area.

Taking the differential of Eq. (3.189) and moving all terms to the left side, we obtain

$$\mathrm{d}E_{i\alpha} - \theta_\alpha \mathrm{d}\eta_{i\alpha} - \gamma_\alpha \mathrm{d}X_{i\alpha} - \mu_{i\alpha}\mathrm{d}\left(\rho_\alpha \omega_{i\alpha}\right) - \rho_\alpha \omega_{i\alpha} \left.\left(\mathrm{d}\mu_{i\alpha}\right)\right|_{\gamma_\alpha,\theta_\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I} \,. \tag{3.191}$$

The species-based Gibbs-Duhem equation is

$$\rho_\alpha \omega_{i\alpha}\mathrm{d}\mu_{i\alpha} + \eta_{i\alpha}\mathrm{d}\theta_\alpha + X_{i\alpha}\mathrm{d}\gamma_\alpha - \rho_\alpha \omega_{i\alpha} \left.\left(\mathrm{d}\mu_{i\alpha}\right)\right|_{\gamma_\alpha,\theta_\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I} \,. \tag{3.192}$$

3.10.4 Common Curve

Common curve results are virtually the same as those for the interface with differences residing in the sign on tension, use of length instead of area, and the fact that densities that arise are per unit length. The Euler equation, differential, and Gibbs-Duhem equations, provided without derivations, are

$$E_{i\alpha} = \theta_\alpha \eta_{i\alpha} - \gamma_\alpha X_{i\alpha} + \rho_\alpha \omega_{i\alpha}\mu_{i\alpha} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{C} \,, \tag{3.193}$$

where

$$X_{i\alpha} = \rho_\alpha \omega_{i\alpha}\overline{L}_{i\alpha} \,; \tag{3.194}$$

$$\mathrm{d}E_{i\alpha} - \theta_\alpha \mathrm{d}\eta_{i\alpha} + \gamma_\alpha \mathrm{d}X_{i\alpha} - \mu_{i\alpha}\mathrm{d}\left(\rho_\alpha \omega_{i\alpha}\right) - \rho_\alpha \omega_{i\alpha} \left.\left(\mathrm{d}\mu_{i\alpha}\right)\right|_{\gamma_\alpha,\theta_\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{C} \,; \tag{3.195}$$

and

$$\rho_\alpha \omega_{i\alpha}\mathrm{d}\mu_{i\alpha} + \eta_{i\alpha}\mathrm{d}\theta_\alpha - X_{i\alpha}\mathrm{d}\gamma_\alpha - \rho_\alpha \omega_{i\alpha} \left.\left(\mathrm{d}\mu_{i\alpha}\right)\right|_{\gamma_\alpha,\theta_\alpha} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{C} \,. \tag{3.196}$$

3.11 Classical Irreversible Thermodynamics (CIT)

In the preceding portions of this chapter, we have rather briefly developed some basic relations that apply to a system at equilibrium. We have noted that in considering equilibrium for a phase, an interface, or a common curve, the intensive properties of the entity are uniform. We have written equilibrium thermodynamic relations for these entities both in terms of the extensive properties of the system (e.g., $\mathbb{E}$, $\mathbb{S}$, $\mathbb{V}$, and $\mathbb{M}_i$ for a fluid phase) and in terms of the densities of the extensive properties (E, η, and $\rho\omega_i$). The differential operator "d" that appears in some of the equations developed refers to infinitesimal changes in quantities as a system transitions between equilibrium states. These equilibrium relations are useful, but the requirement of studying systems at equilibrium presents a serious constraint if one is concerned with dynamic, evolving systems.

Consider the concept of temperature, defined for a phase in Eq. (3.19), based on the change in the functional form of equilibrium internal energy with respect to entropy. With the requirement of equilibrium, the idea of "temperature" has no meaning when a system is not at equilibrium such that its "measure of hotness" varies with time and space. If the equilibrium requirement is enforced, then we cannot talk about the daytime temperature at an outdoor location, or the temperature of a roast in the oven, or of virtually any object not contained in a highly controlled environment. Thus, to make thermodynamics relevant for dynamic systems, we have to be able to relax the constraints of equilibrium without compromising the utility of the framework for some range of problems. This relaxed system is defined by classical irreversible thermodynamics, CIT.

CIT is an assumed extension to equilibrium thermodynamics that generalizes it for application to irreversible processes. This approach has been expounded upon with insight and rigor by de Groot and Mazur [11]. Inherent in this approach is the stipulation that deviation from an equilibrium state be "small" where small is meant to be close enough to equilibrium that CIT applies. The idea behind this approach is that at any point in the system, the functional dependence of $\mathbb{E}^*$ determined from equilibrium analysis applies, even when the system is not at equilibrium. The values of the independent, and thus dependent, variables need not be constant. The formulation is made in terms of property densities, rather than properties of the system as a whole.

For instance, if we consider a fluid phase, the functional form that applies is Eq. (3.40) at any point and time such that

$$E_\alpha = \mathbb{E}^*_\alpha[\eta_\alpha(\mathbf{x},t), 1, \mathcal{R}_\alpha(\mathbf{x},t)] \quad \text{for } \alpha \in \mathcal{I}_\mathrm{f} \,. \tag{3.197}$$

Thus the energy per volume will be a function of position and time through the dependence of entropy and mass densities on position and time. Furthermore, the intensive variables will also be functions of space and time.

The assumption that underlies CIT is referred to as the local equilibrium assumption. In essence it states that each part of a system under consideration can be considered at each moment in time to be in thermal equilibrium. With this assumption, the differentials need not just refer to transitions between equilibrium states but also can be changes occurring at a point with variability in time and space included. Therefore, Eq. (3.41) can be written as a time derivative at a point for a fluid phase as

$$\frac{\partial E_\alpha}{\partial t} = \theta_\alpha \frac{\partial \eta_\alpha}{\partial t} + \sum_{i\in\mathcal{I}_s} \mu_{i\alpha} \frac{\partial(\rho_\alpha \omega_{i\alpha})}{\partial t} \quad \text{for } \alpha \in \mathcal{I}_\mathrm{f} \,. \tag{3.198}$$

Additionally, the differential may be considered to be a spatial derivative such that

$$\nabla E_\alpha = \theta_\alpha \nabla \eta_\alpha + \sum_{i\in\mathcal{I}_s} \mu_{i\alpha} \nabla(\rho_\alpha \omega_{i\alpha}) \quad \text{for } \alpha \in \mathcal{I}_\mathrm{f} \,. \tag{3.199}$$

The influence of time can be understood in the context of a thermometer. A thermometer will give an accurate reading of a varying temperature at a location if it equilibrates quickly enough with the temperature at the point where the measurement is being taken. In other words, specification of the temperature accurately by the thermometer occurs if the thermometer is at equilibrium with the conditions at the point as they are changing. If the temperature changes too quickly, the local equilibrium assumption between the medium and the thermometer will be violated. If the temperature is changing extraordinarily quickly, the definition of temperature itself for the medium may not be possible. This latter case is typically not an issue for porous medium systems, but could come into play, for example, when an explosion or if a fracturing event occurs. Similar scenarios can be envisioned for pressure and chemical potential.

The ability to incorporate spatial variability into a theory is important for processes such as boiling water on a stove, observing the spread of a contaminant in a solvent, and flow caused by a pressure gradient. In these cases, if the equilibrium functional form is satisfied at a point, and the variability from point to point is smooth, then non-equilibrium spatial dependence within the system can be modeled.

If one considers thermodynamic relations for interfaces or common curves at the microscale, it is important to recognize that time or space differentials must be constrained to be on the surface or curve of interest. For example, consider the differential of surface energy given in Eq. (3.148). This equation can be expressed in terms of differentials of extensive quantities per unit area by selection of $\lambda = 1/\mathbb{A}$. Then the partial time derivative constrained to remain on the surface is

$$\frac{\partial' E_\alpha}{\partial t} = \theta_\alpha \frac{\partial' \eta_\alpha}{\partial t} + \sum_{i \in \mathfrak{I}_s} \mu_{i\alpha} \frac{\partial' (\rho_\alpha \omega_{i\alpha})}{\partial t} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I} \,. \tag{3.200}$$

In developing closure relations for conservation and balance equations, we will see that material derivatives of the thermodynamic identities will be useful. Such derivatives are simple combinations of a partial time derivative added to a velocity dotted with the gradient of a quantity. For convenience, and easy access, the forms that may come in handy are collected in Table 3.1. All the equations in the table are obtained by replacing the differential of an Euler equation with the material derivative of the Euler equation, a replacement that is consistent with the local equilibrium assumption of CIT.

The second law of thermodynamics deals with the observation that an irreversible transition between equilibrium states of a system produces entropy globally. Based on CIT, the assumption is made that during the transition between equilibrium states, when a system is undergoing dynamic change, the rate of entropy production of each subsystem of the total system is non-negative. This extension of equilibrium thermodynamics facilitates the derivation of closure relations for some processes in dynamic systems that are not described by conservation or evolution equations. Within the CIT framework, systems are considered to have no memory so that the thermodynamic state of the system at any instant and at any location is described by the equilibrium functional form (e.g., Eq. (3.197) for a fluid phase).

Table 3.1 Material derivatives of thermodynamic Euler equations for use in CIT formulation. The first four rows are for species-based energy equations. Rows five through eight are entity-based. The last four rows may each be obtained as a summation over all species for the corresponding entity. All equations may be obtained from the energy differential expressions in Chap. 3

Material Derivatives of Euler Equations	
Entity	Expression
$\alpha \in \mathfrak{I}_{\mathrm{f}}$	$\mathcal{T}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha} E_{i\alpha}}{\mathrm{D}t} - \theta_\alpha \frac{\mathrm{D}_{i\alpha} \eta_{i\alpha}}{\mathrm{D}t} + p_\alpha \frac{\mathrm{D}_{i\alpha} X_{i\alpha}}{\mathrm{D}t} - \mu_{i\alpha} \frac{\mathrm{D}_{i\alpha} (\rho_\alpha \omega_{i\alpha})}{\mathrm{D}t} - \rho_\alpha \omega_{i\alpha} \left(\frac{\mathrm{D}_{i\alpha} \mu_{i\alpha}}{\mathrm{D}t} \right) \Big\rvert_{p_\alpha, \theta_\alpha} = 0$
s	$\mathcal{T}_{*is} = \frac{\mathrm{D}_{is} E_{is}}{\mathrm{D}t} - \theta_s \frac{\mathrm{D}_{is} \eta_{is}}{\mathrm{D}t} - \boldsymbol{\sigma}_s : \frac{\mathrm{D}_{is}}{\mathrm{D}t} \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) - \mu_{is} \frac{\mathrm{D}_{is} (\rho_s \omega_{is})}{\mathrm{D}t} - \rho_s \omega_{is} \left(\frac{\mathrm{D}_{is} \mu_{is}}{\mathrm{D}t} \right) \Big\rvert_{\boldsymbol{\sigma}_s, \theta_s} = 0$
$\alpha \in \mathfrak{I}_{\mathrm{I}}$	$\mathcal{T}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha} E_{i\alpha}}{\mathrm{D}t} - \theta_\alpha \frac{\mathrm{D}_{i\alpha} \eta_{i\alpha}}{\mathrm{D}t} - \gamma_\alpha \frac{\mathrm{D}_{i\alpha} X_{i\alpha}}{\mathrm{D}t} - \mu_{i\alpha} \frac{\mathrm{D}_{i\alpha} (\rho_\alpha \omega_{i\alpha})}{\mathrm{D}t} - \rho_\alpha \omega_{i\alpha} \left(\frac{\mathrm{D}_{i\alpha} \mu_{i\alpha}}{\mathrm{D}t} \right) \Big\rvert_{\gamma_\alpha, \theta_\alpha} = 0$
$\alpha \in \mathfrak{I}_{\mathrm{C}}$	$\mathcal{T}_{*i\alpha} = \frac{\mathrm{D}_{i\alpha} E_{i\alpha}}{\mathrm{D}t} - \theta_\alpha \frac{\mathrm{D}_{i\alpha} \eta_{i\alpha}}{\mathrm{D}t} + \gamma_\alpha \frac{\mathrm{D}_{i\alpha} X_{i\alpha}}{\mathrm{D}t} - \mu_{i\alpha} \frac{\mathrm{D}_{i\alpha} (\rho_\alpha \omega_{i\alpha})}{\mathrm{D}t} - \rho_\alpha \omega_{i\alpha} \left(\frac{\mathrm{D}_{i\alpha} \mu_{i\alpha}}{\mathrm{D}t} \right) \Big\rvert_{\gamma_\alpha, \theta_\alpha} = 0$
$\alpha \in \mathfrak{I}_{\mathrm{f}}$	$\mathcal{T}_{*\alpha} = \frac{\mathrm{D}_\alpha E_\alpha}{\mathrm{D}t} - \theta_\alpha \frac{\mathrm{D}_\alpha \eta_\alpha}{\mathrm{D}t} - \sum_{i \in \mathfrak{I}_s} \mu_{i\alpha} \frac{\mathrm{D}_\alpha (\rho_\alpha \omega_{i\alpha})}{\mathrm{D}t} = 0$
s	$\mathcal{T}_{*s} = \frac{\mathrm{D}_s E_s}{\mathrm{D}t} - \theta_s \frac{\mathrm{D}_s \eta_s}{\mathrm{D}t} - \boldsymbol{\sigma}_s : \frac{\mathrm{D}_s}{\mathrm{D}t} \left(\frac{\mathbf{C}_s}{j_s} \right) - \sum_{i \in \mathfrak{I}_s} \mu_{is} \frac{\mathrm{D}_s (\rho_s \omega_{is})}{\mathrm{D}t} = 0$
$\alpha \in \mathfrak{I}_{\mathrm{I}}$	$\mathcal{T}_{*\alpha} = \frac{\mathrm{D}_\alpha E_\alpha}{\mathrm{D}t} - \theta_\alpha \frac{\mathrm{D}_\alpha \eta_\alpha}{\mathrm{D}t} - \sum_{i \in \mathfrak{I}_s} \mu_{i\alpha} \frac{\mathrm{D}_\alpha (\rho_\alpha \omega_{i\alpha})}{\mathrm{D}t} = 0$
$\alpha \in \mathfrak{I}_{\mathrm{C}}$	$\mathcal{T}_{*\alpha} = \frac{\mathrm{D}_\alpha E_\alpha}{\mathrm{D}t} - \theta_\alpha \frac{\mathrm{D}_\alpha \eta_\alpha}{\mathrm{D}t} - \sum_{i \in \mathfrak{I}_s} \mu_{i\alpha} \frac{\mathrm{D}_\alpha (\rho_\alpha \omega_{i\alpha})}{\mathrm{D}t} = 0$

The CIT approach has been used with great success for the situation where each subsystem is a microscale point. However, its application at a larger scale must be undertaken with caution. For instance, for a system as a whole in which spatial and temporal variability of thermodynamic quantities must be accounted for, the assumption of "local" equilibrium, with the "locality" being the entire system, clearly does not apply. Besides the inherent mathematical complications, physically one can understand that there is no unique way to define intensive thermodynamic variables that characterize a non-uniform system [14].

The problem of defining physically and mathematically reasonable thermodynamic variables at the macroscale appropriate for analysis of porous medium systems is also challenging when the variable is not constant at the macroscale. The TCAT approach addresses this problem by directly averaging the microscale thermodynamic relations and then modeling in terms of the averages of these variables that arise. This circumvents the need to employ ad hoc macroscale functional forms for energy that lead to variables unrelated to the basic tenets of equilibrium thermodynamics and which rely on some axioms that are controversial at the microscale and become more problematic at a larger scale [33, 35, 39, 54–56]. In cases where the local equilibrium assumption applies at a macroscale locality, the issue of accounting for subscale variability is eliminated.

Recall that from a microscale perspective, the boundaries of a phase are well defined. This does not preclude a system from being comprised of more than one phase. When multiple phases exist, specification of the conditions that apply at equilibrium becomes more complicated because of the presence of interfaces and common curves that support discontinuities in properties between phases and which, in their own right, impact the system behavior. Additionally, the impact of external potentials, such as gravity, must be accounted for in a thermodynamic theory capable of describing the porous medium systems of interest. A thorough examination of the microscale equilibrium conditions for these systems is the topic of the next chapter.

3.12 Other Thermodynamic Theories

Thermodynamic theories provide supplemental constraints to the conservation and balance equations developed in Chap. 2. When employing the TCAT approach, we average the thermodynamic relations expressed in terms of microscale variables to a larger scale. Any consistent microscale thermodynamic theory can be employed. However, it is important that the thermodynamic relations not be postulated directly at the larger scale when the system is not at equilibrium because the meaning of the new thermodynamic variables would be ambiguous.

In subsequent chapters, we employ CIT as described in section 3.11 because it is the simplest extension beyond equilibrium thermodynamics that also provides some useful results. However, because other thermodynamic approaches may also be employed, some are mentioned here along with their features, as in [20]. Incorporation of these approaches is feasible in the TCAT framework and may assist in model development when the particular features of the thermodynamic theory are important in describing the material properties.

3.12.1 Rational Thermodynamics (RT)

Rational thermodynamics (RT) [9, 13, 23, 43, 46, 52, 54] is a class of thermodynamic approaches. In brief, RT and its extensions make use of an expanded set of independent variables that energy depends upon and that also accounts for the impact of the path of change of the system. This approach has proven to be a useful component of methods for deriving constitutive equations [26]. The method is mathematically rigorous and is built on principles that lead to certain mathematical forms for the energy and constitutive functions [13]. Although the principles have some mathematical appeal, it has been pointed out that they are actually only working hypotheses [39] or useful rules [54]. Among these rules are the requirement that if an independent variable is present in one of the constitutive equations, it must initially be presumed to be present in all. The rule of memory states that present effects are dictated by past as well as present values of independent variables.

Rational mechanics has provided some advances in obtaining general closure relations for complex solids. For modeling porous medium systems, the two rules mentioned above impose some generality that is needlessly complicated. Of greater concern is the fact that RT assumes notions that are precisely defined in equilibrium thermodynamics to exist in any dynamic state. In RT, absolute temperature and entropy are considered to be primitive concepts that are believed to apply far from equilibrium; but they have no precise physical interpretation or physical relation to their ET counterparts [39]. Materials are allowed to have a memory, and the concept of local equilibrium is not necessarily enforced. The absence of correspondence of variables in RT with those defined classically is further complicated in porous media studies when the variables are introduced at a larger scale. Inherently, the relations between some variables across scales is absent such that the RT framework can lead to a mathematically elegant but physically lacking equation set.

3.12.2 Extended Irreversible Thermodynamics (EIT)

Extended irreversible thermodynamics (EIT) [27–31, 34, 35, 38, 42, 45] is an approach to microscale thermodynamics that extends the local equilibrium assumption employed with CIT by also allowing internal energy to depend on the local dissipative fluxes. This approach tries to account for shorter wave length and high frequency phenomena. At equilibrium the fluxes will be zero. Thus at equilibrium, or when the dependence on these fluxes is small, the EIT formulation is identical to CIT. The range of applicability of EIT non-equilibrium thermodynamics is considered to be broader than that obtained with CIT because memory, non-local, and non-linear effects are incorporated into the formulation through the extended dependence of energy on fluxes. The extension of this approach to the macroscale for cases of large dissipative fluxes may be possible if the microscale EIT formulation can be consistently averaged.

3.12.3 Theory of Internal Variables (TIV)

The theory of internal variables (TIV) [10, 37, 39, 40, 53] has been developed to model systems that have internal structure and is most often applied to nonlinear materials. The idea behind this method is to expand the dependence of energy on independent variables to include some that provide measures of that internal structure. Thus the approach can be considered to be an extension of CIT that adds some state variables to the set that is traditionally employed based on classical equilibrium thermodynamic considerations. The classic intensive variables are considered controllable or observable while the newly introduced independent variables are not. Rather, these internal variables of state describe the internal structure hidden from the observer. Appropriate and astute selection of these internal variables depends heavily on the scale at which the system is being observed and the dissipative behavior that is being modeled. The expansion of the list of variables at the microscale has some similarities to systematic transformation of CIT to a macroscale wherein internal variables relating to the geometric properties arise naturally. However, application of TIV to porous medium systems would require that the additional variables added at the microscale be transformed to the larger scale.

3.13 Summary

In this chapter, we have introduced some basic elements of microscale thermodynamics. Thermodynamics plays a central role in the development of TCAT models and is used for establishing conditions that proposed closure relations must necessarily satisfy. While the field of thermodynamics is immense, we have presented the essence of equilibrium thermodynamics as developed from a postulational approach. Subsequently, we introduced classical irreversible thermodynamics as an extension of equilibrium thermodynamics. Using CIT, one can model the variability of thermodynamic quantities in time and space. This approach is built on the hypothesis that the functional forms, useful in describing equilibrium systems, can be applied unaltered for systems away from equilibrium. This hypothesis is referred to as the local equilibrium assumption.

In this introduction, focus has been on the establishment of Euler and Gibbs-Duhem equations, as well as on the definitions of intensive thermodynamic variables. This has been accomplished for fluid and solid phases, interfaces between phases, and common curves where three phases meet. The local equilibrium extension to equilibrium thermodynamics has been experimentally verified in studies of many physical systems. The CIT formulation is the one that will be averaged subsequently in the TCAT framework to increase the scale at which a system is modeled. Averaging assures that the thermodynamic formulation at the larger scale is consistent with smaller scale definitions of variables and with the tenets of thermodynamics. In some systems where gradients or fluxes are large or rapidly varying in time, it may be necessary to build the thermodynamic formalism on a more complex foundation than CIT. Some alternatives have been mentioned, but they will not be explored further here.

This chapter does not delve into applications, determination of state equations, measurement approaches, or considerations that are important for ascertaining the most advantageous thermodynamic formulation for a given system (i.e., which elements of the system must be explicitly modeled). These topics are important for a complete implementation of thermodynamic principles and describing the behavior of single and multiphase systems. However, only the thermodynamic issues of immediate need for the objectives of this book have been introduced. For a more comprehensive introduction to thermodynamic theory, which is recommended, some excellent texts devoted to that topic are available [1, 8, 11, 35, 39].

Exercises

3.1. Consider the normalized internal energy function for a fluid phase α as discussed in Sect. 3.4. In this exercise, the energy will be normalized with respect to the mass of the system by selecting $\lambda = 1/\mathbb{M}_\alpha$. Denote the energy per mass of the phase as e_α and the entropy per mass as s_α.

a. Obtain the Euler form of the energy equation.
b. Show that the differential form of the Euler equation is

$$\mathrm{d}e_\alpha = \theta_\alpha \,\mathrm{d}s_\alpha + \frac{p_\alpha}{\rho_\alpha^2}\,\mathrm{d}\rho_\alpha + \sum_{i\in\mathfrak{I}_s} \mu_{i\alpha}\,\mathrm{d}\left(\omega_{i\alpha} - \omega_{N\alpha}\right) \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{f}\,, \tag{3.201}$$

where the subscript N refers to one of the chemical species present chosen as a reference species.
c. Find the general functional forms of the equations of state needed to complete the thermodynamic description of fluid phase α.
d. Obtain the Gibbs-Duhem equation for this phase and show that it is consistent with Eq. (3.43).

3.2. Based on the definition of the Helmholtz free energy for a fluid phase given as Eqs. (3.62)–(3.69), find the Gibbs-Duhem equation and determine if it is consistent with Eq. (3.43) obtained when working with the internal energy function.

3.3. Derive Eq. (3.122) starting from the differential of the equation of state encountered in working with the Gibbs free energy as Eq. (3.99).

3.4. Transform the internal energy equation for a solid phase to an expression for the enthalpy. Give expressions for the enthalpy, the differential of enthalpy, the equations of state, and the Gibbs-Duhem equation.

3.5. Derive the relation between $\mathbb{C}_P$ and $\mathbb{C}_V$ for a solid.

3.6. Show that the interfacial tension for a surface may be defined equivalently to Eq. (3.146) as

$$\gamma_\alpha = \left(\frac{\partial \mathbb{F}^*_\alpha}{\partial \mathbb{A}_\alpha}\right)_{\theta_\alpha,\mathbb{M}_\alpha} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I}\,. \tag{3.202}$$

3.7. Show that for a massless interface, the interfacial tension is equal to the Helmholtz free energy density.

3.8. The grand canonical potential is another potential that can be employed in thermodynamic analysis. Denote it as $\mathbb{P}_\alpha$ where, for a phase,

$$\lambda\mathbb{P}_\alpha = \lambda\mathbb{E}_\alpha - \theta_\alpha\lambda\mathbb{S}_\alpha - \sum_{i\in\mathfrak{I}_s} \mu_{i\alpha}\lambda\mathbb{M}_{i\alpha} \quad \text{for } \alpha \in \mathfrak{I}\,. \tag{3.203}$$

a. If $\lambda\mathbb{P}_\alpha = \mathbb{P}^*_\alpha$ where $\alpha \in \mathcal{I}_\mathrm{f}$, determine the Euler form for $\lambda\mathbb{P}_\alpha$ and the fundamental independent variables on which $\mathbb{P}^*_\alpha$ depends.
b. if $\lambda\mathbb{P}_s = \mathbb{P}^*_s$, determine the Euler form for $\lambda\mathbb{P}_s$ and the independent variables on which $\mathbb{P}^*_s$ depends.
c. Show that for a massless common curve, $P_\alpha = -\gamma_\alpha$ for $\alpha \in \mathcal{I}_\mathrm{C}$ where P_α is the grand canonical potential per unit length of common curve.

3.9. Show that

$$\mathrm{d}\mu_{i\alpha} = \left.\mathrm{d}\mu_{i\alpha}\right|_{\theta_\alpha} + \theta_\alpha \left(\overline{H}_{i\alpha} - \mu_{i\alpha}\right) \mathrm{d}\left(\frac{1}{\theta_\alpha}\right) \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_\mathrm{f}\,. \tag{3.204}$$

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Chapter 4
Microscale Equilibrium Conditions

4.1 Overview

The role of classical thermodynamics is to represent the equilibrium state of a system and the change in system properties that occurs due to a transition between states. Because the TCAT method describes system dynamics at "near" equilibrium dynamic conditions, it is essential to know what the actual equilibrium conditions are. The second law of equilibrium thermodynamics requires that entropy production associated with a spontaneous, irreversible change of system state be non-negative. When CIT is employed as the thermodynamic framework, this statement transforms to a requirement that the rate of entropy generation be non-negative at all times for a dynamic system. Since TCAT involves the description of dynamic systems near equilibrium, we need to ensure that the closure relations used to describe irreversible processes are consistent with the principle of non-negative entropy generation. By having knowledge of the conditions that must apply at equilibrium, we will be able to develop consistent closure relations.

The purpose of this chapter is to formulate equilibrium conditions for microscale systems of varying complexity, where the complexity results from juxtaposed phases, interfaces, common curves, and common points. The approach to obtaining these conditions is based on variational analysis of the total energy of a system. This analysis is based on the fact that at equilibrium, a system is at a minimum energy state. Therefore, any perturbation of independent variables that describe this state must result in no change in energy. This is analogous to saying that the slope of a function is zero at its minimum. To facilitate the analysis, we will consider expressions for the variation of independent system variables and also variational analysis of integral functionals. The emphasis here is on utilizing the expressions that result to develop conditions of equilibrium for a multiphase system. Derivation of the elements of variational calculus employed here may be found in the literature [7, 8, 18]. Some of the underlying theory is provided in Appendix A of this book along with the derivation of three variational theorems that will be employed in this work. This chapter provides an explanation of the rationale behind using a varia-

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tional approach to obtain equilibrium conditions as well as some useful variational relations. These will be employed to develop equilibrium conditions for a single fluid phase and for two fluids in an elastic porous medium. Besides developing conditions that will prove to be useful for closure of TCAT models, the manipulations also demonstrate the approach that can be employed if alternative thermodynamic formalisms are proposed.

4.2 Components of Variational Analysis

With classical thermodynamics, equilibrium conditions for a homogeneous system are often developed from thermal, chemical, and mechanical considerations of system behavior [e.g., 6, 9, 10, 14, 16]. For more complex systems, such as multiphase porous medium systems with deformable solids, interfaces, and common curves, the challenges to determining equilibrium conditions are more significant. To respond to this challenge, we will employ variational methods to derive a full set of microscale equilibrium conditions. The analysis here will be restricted to systems whose individual entities can be described using CIT, as described in Chap. 3.

Variational methods are widely used to solve optimization problems in which an integral of a functional is posed such that a minimum to a problem of interest is determined. Variational principles are also described as replacing local rules with global conditions that can then be exploited to obtain the local conditions [8]. It is this latter perspective that we will be employing. We will provide expressions for the total energy of a multiphase system and then make use of variational manipulations to determine what local conditions are implied by a requirement of equilibrium. In particular, we will make use of the fact that thermodynamic equilibrium implies that a system is at a state of minimum energy. Because the change in energy with respect to perturbations in the independent variables at equilibrium will thus be zero, examination of the perturbations around the equilibrium state will provide relations among variables at equilibrium.

The application here is related to the roots of variational analysis in that we will seek a minimum of a functional posed in terms of an integral expression. This use is different from usual applications of basic variational methods in that the expression we wish to minimize involves a sum of integrals over different types of entities (volumes, interfaces, and common curves), subject to a set of constraints. Fundamental aspects and relations of variational analysis that are important for our derivation are considered for volumes, interfaces, and curves in Appendix A. The mathematical results found there are used to develop the microscale equilibrium conditions for a multiphase system in the present chapter. Variational methods have been used to determine equilibrium conditions for systems involving interfaces, common curves, and common points [2–4], although we will consider a somewhat simpler case in which the effects of interface and common curve curvature on the internal energy density are neglected [11, 12, 15].

The variational analysis will require two sets of information. The first is expressions for the variation of microscale quantities that will be integrated over their appropriate domains. The second is the set of equalities that relate the variation of an integral to the integral of the variation of an integrand. These two sets of equalities are summarized here based on the understanding of variational methods from Appendix A and the derivations therein.

4.3 Variation of Microscale Quantities

A variational analysis of an integral leads to formulation of expressions for variations of variables that appear in the integrand under study. Some of these variables, such as the entropy per volume for a phase, are independent quantities, and their variations remain in the analysis. However, the variation of other variables, such as phase density, gravitational potential, and the Green's deformation tensor, can be related to changes in other quantities. These other changes are primarily related to a variation in position, and these interrelations must be specified. Variational analysis requires that independent variations be scrutinized. Thus, it is important to ensure that the variations of microscale variables that appear in the analysis are indeed independent. Some of the important and useful relations are collected in Table 4.1. For clarity, $\delta\mathbf{x}$ in the table is subscripted with the indicator of the entity being considered.

Although the derivation of the relations, for the most part, will not be provided here, it may be helpful to note that the expressions are very similar to those that are obtained in taking time derivatives. Correspondence is obtained if one replaces the variational operator with a material derivative, a fixed point operator with a partial time derivative, and $\delta\mathbf{x}$ with a velocity. This correspondence should not be too surprising as it has been pointed out that a variation is akin to a derivative [7].

At this point, we are peeking ahead with an eye toward providing the relations that will be needed when performing variational analysis of the system energy. Not all of the relations that appear in Table 4.1 will be needed for all problems; some of them will not be needed for any of the analyses performed here. Nevertheless, the relations do provide a basic set of tools if one wishes to study a more complex thermodynamic formulation for energy. As an example calculation of one of the entries in the table, we study the Green's strain tensor.

4.3.1 Variation of Green's Strain Tensor

The Green's deformation tensor—also known as the right Cauchy-Green deformation tensor C_s—appears in the expression for the internal energy of the solid per unit volume as in Eq. (3.159). Strain involves deformation of the solid; and a change in volume is accounted for by the jacobian, j_s. Therefore, some common features of

Table 4.1 Collection of expressions for the variation of various microscale functions associated with phases, interfaces, and common curves for subsequent use in analysis of equilibrium conditions

Domain	**Quantity**	**Expression**
	Fixed-point Variation	$\overline{\delta} f_\alpha = \delta f_\alpha - \delta\mathbf{x}_\alpha \cdot \nabla f_\alpha$
	Fluid Energy Density	$\overline{\delta} E_\alpha = \theta_\alpha \overline{\delta}\eta_\alpha + \sum\limits_{i\in\mathfrak{I}_s} \mu_{i\alpha}\overline{\delta}(\rho_\alpha\omega_{i\alpha})$
Phase	Solid Energy Density	$\overline{\delta} E_s = \theta_s \overline{\delta}\eta_s + \boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathsf{C}_s}{j_s}\right) + \sum\limits_{i\in\mathfrak{I}_s} \mu_{is}\overline{\delta}(\rho_s\omega_{is})$
$\alpha \in \mathfrak{I}_\mathrm{P}$	Mass Density	$\delta\rho_\alpha = -\rho_\alpha \nabla\cdot\delta\mathbf{x}_\alpha$
	Gravitational Potential	$\overline{\delta}\psi_\alpha = 0$
	Jacobian	$\delta j_\alpha = j_\alpha \nabla\cdot\delta\mathbf{x}_\alpha$
	Green's Strain	$\overline{\delta}\mathsf{C}_s = \nabla_X \mathbf{x}_s \cdot \left(\nabla(\delta\mathbf{x}_s) + [\nabla(\delta\mathbf{x}_s)]^\mathrm{T}\right)\cdot(\nabla_X\mathbf{x}_s)^\mathrm{T}$
	Fixed-point Variation	$\overline{\delta}' f_{\alpha\beta} = \delta f_{\alpha\beta} - \delta\mathbf{x}_{\alpha\beta}\cdot\nabla' f_{\alpha\beta}$
	Energy Density	$\overline{\delta}' E_{\alpha\beta} = \theta_{\alpha\beta}\overline{\delta}'\eta_{\alpha\beta} + \sum\limits_{i\in\mathfrak{I}_s} \mu_{i\alpha\beta}\overline{\delta}'(\rho_{\alpha\beta}\omega_{i\alpha\beta})$
Interface	Gravitational Potential	$\overline{\delta}'\psi_{\alpha\beta} = -\mathbf{g}_{\alpha\beta}\cdot\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\beta} = -\mathbf{g}_{\alpha\beta}\cdot\left(\mathsf{I} - \mathsf{I}'_{\alpha\beta}\right)\cdot\delta\mathbf{x}_{\alpha\beta}$
$\alpha\beta \in \mathfrak{I}_\mathrm{I}$	Unit Normal	$\delta\mathbf{n}_\alpha = -\left(\nabla'\delta\mathbf{x}_{\alpha\beta}\right)\cdot\mathbf{n}_\alpha$
	Surface Tensor	$\delta\mathsf{I}'_{\alpha\beta} = \mathbf{n}_\alpha\nabla'\delta\mathbf{x}_{\alpha\beta}\cdot\mathbf{n}_\alpha + \left(\mathbf{n}_\alpha\nabla'\delta\mathbf{x}_{\alpha\beta}\cdot\mathbf{n}_\alpha\right)^\mathrm{T}$
	First Curvature $J_{\alpha\beta} = \nabla'\cdot\mathbf{n}_\alpha$	$\overline{\delta}' J_{\alpha\beta} = -\left(\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\beta}\right)\left(J^2_{\alpha\beta} - 2K_{\alpha\beta}\right) - \nabla'\cdot\left[\nabla'\left(\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\beta}\right)\right]$
	Second Curvature $K_{\alpha\beta} = \frac{1}{2}\left(J^2_{\alpha\beta} - \nabla'\mathbf{n}_\alpha{:}\nabla'\mathbf{n}_\alpha\right)$	$\overline{\delta}' K_{\alpha\beta} = -\left(\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\beta}\right)K_{\alpha\beta}J_{\alpha\beta} - \left(J_{\alpha\beta}\mathsf{I}'_{\alpha\beta} - \nabla'\mathbf{n}_\alpha\right){:}\nabla'\left[\nabla'\left(\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\beta}\right)\right]$
	Fixed-point Variation	$\overline{\delta}'' f_{\alpha\beta\gamma} = \delta f_{\alpha\beta\gamma} - \delta\mathbf{x}_{\alpha\beta\gamma}\cdot\nabla'' f_{\alpha\beta\gamma}$
Common	Energy Density	$\overline{\delta}'' E_{\alpha\beta\gamma} = \theta_{\alpha\beta\gamma}\overline{\delta}''\eta_{\alpha\beta\gamma} + \sum\limits_{i\in\mathfrak{I}_s} \mu_{i\alpha\beta\gamma}\overline{\delta}''(\rho_{\alpha\beta\gamma}\omega_{i\alpha\beta\gamma})$
Curve	Gravitational Potential	$\overline{\delta}''\psi_{\alpha\beta\gamma} = -\mathbf{g}_{\alpha\beta\gamma}\cdot\left(\mathsf{I} - \mathbf{l}_{\alpha\beta\gamma}\mathbf{l}_{\alpha\beta\gamma}\right)\cdot\delta\mathbf{x}_{\alpha\beta\gamma} = -\mathbf{g}_{\alpha\beta\gamma}\cdot\left(\mathsf{I} - \mathsf{I}''_{\alpha\beta\gamma}\right)\cdot\delta\mathbf{x}_{\alpha\beta\gamma}$
$\alpha\beta\gamma \in \mathfrak{I}_\mathrm{C}$	Unit Tangent	$\delta\mathbf{l}_{\alpha\beta\gamma} = \mathbf{l}_{\alpha\beta\gamma}\cdot\nabla''\delta\mathbf{x}_{\alpha\beta\gamma}\cdot\left(\mathsf{I} - \mathbf{l}_{\alpha\beta\gamma}\mathbf{l}_{\alpha\beta\gamma}\right)$
	Curvature $\kappa_{\alpha\beta\gamma} = \mathbf{l}_{\alpha\beta\gamma}\cdot\nabla\mathbf{l}_{\alpha\beta\gamma}$	$\delta\kappa_{\alpha\beta\gamma} = \mathbf{l}_{\alpha\beta\gamma}\cdot\nabla''\left(\mathbf{l}_{\alpha\beta\gamma}\cdot\nabla''\delta\mathbf{x}_{\alpha\beta\gamma}\right) - \mathbf{l}_{\alpha\beta\gamma}\cdot\nabla''\left[\mathbf{l}_{\alpha\beta\gamma}\cdot\left(\nabla''\delta\mathbf{x}_{\alpha\beta\gamma}\right)\cdot\mathbf{l}_{\alpha\beta\gamma}\right]\mathbf{l}_{\alpha\beta\gamma}$

both quantities can be accounted for if $\delta\mathsf{C}_s$ and δj_s are written in terms of $\delta\mathbf{x}_s$ rather than presuming that they are independent variables. The goal of this subsection is to derive the relation between $\delta\mathsf{C}_s$ and $\delta\mathbf{x}_s$ so that the variational problem to be studied can be expressed in terms of a clear set of conditions that must hold at equilibrium.

Recall the definition of the Green's deformation tensor from Eq. (3.131)

$$\mathsf{C}_s = \nabla_X\mathbf{x}_s\cdot\left(\nabla_X\mathbf{x}_s\right)^\mathrm{T} \; . \tag{4.1}$$

We wish to evaluate the fixed-point variation of this tensor. Note that the tensor depends upon a derivative of $\mathbf{x}_s$, the location of a solid particle, with respect to $\mathbf{X}_s$, which is the initial position of the particle. With $\mathbf{X}_s$ not subject to variation, we can seek the variation of C_s. This is the variation of the change of a system from one deformed state to another deformed state without changing the initial configuration.

The variation of C_s can be written as

$$\delta\mathsf{C}_s = \delta\left[\nabla_X\mathbf{x}_s\cdot\left(\nabla_X\mathbf{x}_s\right)^\mathrm{T}\right] \; . \tag{4.2}$$

By the product rule for a variation, expansion of this expression yields

$$\delta \mathsf{C}_s = \delta \left(\nabla_X \mathbf{x}_s\right) \cdot \left(\nabla_X \mathbf{x}_s\right)^{\mathrm{T}} + \nabla_X \mathbf{x}_s \cdot \delta \left[\left(\nabla_X \mathbf{x}_s\right)^{\mathrm{T}}\right] . \tag{4.3}$$

The order of the differentiation and variational operators may be interchanged to obtain

$$\delta \mathsf{C}_s = \nabla_X \left(\delta \mathbf{x}_s\right) \cdot \left(\nabla_X \mathbf{x}_s\right)^{\mathrm{T}} + \nabla_X \mathbf{x}_s \cdot \left[\nabla_X \left(\delta \mathbf{x}_s\right)\right]^{\mathrm{T}} . \tag{4.4}$$

The variation $\delta \mathbf{x}_s$ is a function of $\mathbf{x}_s \left(\mathbf{X}_s\right)$. Thus, the chain rule shows that

$$\nabla_X \left(\delta \mathbf{x}_s\right) = \nabla_X \mathbf{x}_s \cdot \nabla \left(\delta \mathbf{x}_s\right) , \tag{4.5}$$

which can be used to write Eq. (4.4) as

$$\delta \mathsf{C}_s = \nabla_X \mathbf{x}_s \cdot \nabla \left(\delta \mathbf{x}_s\right) \cdot \left(\nabla_X \mathbf{x}_s\right)^{\mathrm{T}} + \nabla_X \mathbf{x}_s \cdot \left[\nabla \left(\delta \mathbf{x}_s\right)\right]^{\mathrm{T}} \cdot \left(\nabla_X \mathbf{x}_s\right)^{\mathrm{T}} . \tag{4.6}$$

This expression, in turn, may be factored to the expression for the variation of C_s,

$$\delta \mathsf{C}_s = \nabla_X \mathbf{x}_s \cdot \left(\nabla \left(\delta \mathbf{x}_s\right) + \left[\nabla \left(\delta \mathbf{x}_s\right)\right]^{\mathrm{T}}\right) \cdot \left(\nabla_X \mathbf{x}_s\right)^{\mathrm{T}} . \tag{4.7}$$

The fixed point variation of C_s, i.e., the perturbation in C_s imposed at a fixed spatial location, $\mathbf{x}_s$, may be obtained using the definition of a fixed point variation in space of an arbitrary function given in the first line of Table 4.1. The result is

$$\bar{\delta} \mathsf{C}_s = \delta \mathsf{C}_s - \delta \mathbf{x}_s \cdot \nabla \mathsf{C}_s . \tag{4.8}$$

However, $\nabla \mathsf{C}_s = 0$ so that $\delta \mathsf{C}_s = \bar{\delta} \mathsf{C}_s$ and Eq. (4.7) may be written

$$\bar{\delta} \mathsf{C}_s = \nabla_X \mathbf{x}_s \cdot \left(\nabla \left(\delta \mathbf{x}_s\right) + \left[\nabla \left(\delta \mathbf{x}_s\right)\right]^{\mathrm{T}}\right) \cdot \left(\nabla_X \mathbf{x}_s\right)^{\mathrm{T}} . \tag{4.9}$$

Equation (4.9) has been entered for convenience into Table 4.1.

The calculation of some of the other entries in Table 4.1 are left as exercises. The objective here is to utilize the expressions for variations for physical problems rather than provide all the underlying derivations, some of which can be found elsewhere [e.g., 2, 12].

4.4 Variation of Energy Integrals

The objective of this chapter is to provide an approach to determining the thermodynamic conditions that apply to a multiphase system at equilibrium. Although the conditions will be different depending on the specific system under consideration, some general principles apply that suggest an appropriate path of analysis. One condition is that a closed system at equilibrium is at a state of minimum energy such that any perturbations around that state will increase the energy. A second condition is that the entropy of the equilibrium system is at a maximum such that any perturbation in the system away from equilibrium would cause the entropy to decrease. The third condition is that at equilibrium, chemical reactions will cease such that the masses of each of the chemical species will be constant. Any perturbation about the equilibrium state will cause a species mass to either increase or decrease, depending on the reaction. From these observations, the equilibrium state is observed to be one where small variations result in zero change in the total energy and entropy of the system and in zero change of the mass of each chemical species.

Another common feature of the multiphase systems of interest is that they contain multiple entity types. For example, a porous medium system composed of a fluid and solid will consist of two phase entities and an interfacial entity that is the boundary between the two phases. Each of these entities has thermodynamic properties and is described by thermodynamic relations as discussed in Chap. 3. Similarly, a system composed of two fluids and a solid will have three phase entities, three interface entities with each being an interface between a pair of phases, and a common curve where the three interfaces meet. Common points can exist in four-phase systems, but we will not consider such systems here.

For the systems under consideration, the equilibrium conditions of minimum energy, maximum entropy, and fixed mass of each species will apply to the system as a whole, rather than to individual entities, because the entities interact with each other and cannot be treated in isolation. The interaction leads to some conditions that must apply in the interior of a system beyond those conditions obtained for a single phase system. On the interior of a domain, boundaries between entities will adjust their locations and extents (area, length, or number) in reaching an equilibrium state. Equilibrium states may be achieved that have different distributions and morphology of entities. However any equilibrium state must be one of minimum energy, maximum entropy, and unchanging species masses. Because the system as a whole is considered, the situation is complicated because we stipulate only the external boundary of the system, not the boundary of each individual entity within the system. The extent of the entities may vary as may their locations and morphology.

The energy, entropy, and species masses of a system are obtained as integrals over the domain of each entity of the local values expressed on a per unit entity basis. The equilibrium energy is composed of both the internal and the potential energy contributions. Thus, the total system energy, $\mathbb{E}_T$, is

$$\mathbb{E}_T = \sum_{\alpha\in\mathfrak{J}} \int\limits_{\Omega_\alpha} (E_\alpha + \Psi_\alpha)\, \mathrm{d}\mathfrak{r} \,, \tag{4.10}$$

where $\mathfrak{J}$ is the index set of entities and Ω_α is the domain of entity α. The system entropy, $\mathbb{S}_T$, is likewise obtained as an integral of point values over all entities with

$$\mathbb{S}_T = \sum_{\alpha\in\mathfrak{J}} \int\limits_{\Omega_\alpha} \eta_\alpha\, \mathrm{d}\mathfrak{r} \,. \tag{4.11}$$

Table 4.2 Relations for variation of integrals over phases, interface, and common lines as derived in Appendix A. For clarity, the notation $\delta \mathbf{x}_\alpha$ is introduced to denote the variation of a location within the domain of entity α while $\delta \mathbf{x}_{\alpha\alpha}$ is employed to denote the variation of the location of the boundary of entity α

	$\delta F_\alpha = \delta \int_{\Omega_\kappa} f_\alpha \, \mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{J}$	
Domain	**Variational Relation**	**Eq.**
Phase $\alpha \in \mathfrak{J}_\mathrm{P}$	$\delta F_\alpha = \int_{\Omega_\alpha} \overline{\delta} f_\alpha \, \mathrm{d}\mathfrak{r} + \int_{\Gamma_\alpha} f_\alpha \mathbf{n}_\alpha \cdot \delta \mathbf{x}_{\alpha\alpha} \, \mathrm{d}\mathfrak{r}$	(A.53)
Interface $\alpha \in \mathfrak{J}_\mathrm{I}$	$\delta F_\alpha = \int_{\Omega_\alpha} \overline{\delta}' f_\alpha \, \mathrm{d}\mathfrak{r} - \int_{\Omega_\alpha} f_\alpha \nabla' \cdot \mathbf{I}'_\alpha \cdot \delta \mathbf{x}_\alpha \, \mathrm{d}\mathfrak{r} + \int_{\Gamma_\alpha} f_\alpha \mathbf{n}_\alpha \cdot \delta \mathbf{x}_{\alpha\alpha} \, \mathrm{d}\mathfrak{r}$	(A.64)
Common Curve $\alpha \in \mathfrak{J}_\mathrm{C}$	$\delta F_\alpha = \int_{\Omega_\alpha} \overline{\delta}'' f_\alpha \, \mathrm{d}\mathfrak{r} - \int_{\Omega_\alpha} f_\alpha \nabla'' \cdot \mathbf{I}''_\alpha \cdot \delta \mathbf{x}_\alpha \, \mathrm{d}\mathfrak{r} + \sum_{\kappa \in \Gamma_\alpha} \left. (f_\alpha \mathbf{n}_\alpha \cdot \delta \mathbf{x}_{\alpha\alpha}) \right\|_\kappa$	(A.84)
Common Point $\alpha \in \mathfrak{J}_\mathrm{Pt}$	$\delta F_\alpha = \sum_{\kappa \in \Omega_\alpha} \left. \overline{\delta}''' f_\alpha \right\|_\kappa$	inferred

The total mass of chemical species i in the domain, $\mathbb{M}_{iT}$, is obtained as a sum over all entities according to

$$\mathbb{M}_{iT} = \sum_{\alpha \in \mathfrak{J}} \int_{\Omega_\alpha} \rho_\alpha \omega_{i\alpha} \, \mathrm{d}\mathfrak{r} \quad \text{for } i \in \mathfrak{J}_s \, , \tag{4.12}$$

where $\mathfrak{J}_s$ is the index set of chemical species.

Equations (4.10)–(4.12) can be combined to obtain a functional for the system, $\mathbb{F}_T$, defined as

$$\mathbb{F}_T = \mathbb{E}_T - \lambda_\mathbb{S} \mathbb{S}_T - \sum_{i \in \mathfrak{J}_s} \lambda_{\mathbb{M}_i} \mathbb{M}_{iT} \, , \tag{4.13}$$

where $\lambda_\mathbb{S}$ and $\lambda_{\mathbb{M}_i}$ are a set of unspecified constant Lagrange parameters that ensure consistency of units in combining these integrals. We can take the variation of Eq. (4.13) to obtain

$$\delta \mathbb{F}_T = \delta \mathbb{E}_T - \lambda_\mathbb{S} \delta \mathbb{S}_T - \sum_{i \in \mathfrak{J}_s} \lambda_{\mathbb{M}_i} \delta \mathbb{M}_{iT} \, , \tag{4.14}$$

where the variation of the coefficients is zero because they are constants. The functional $\mathbb{F}_T$ has the interesting property that its variation will be zero at equilibrium for any values of $\lambda_\mathbb{S}$ and $\lambda_{\mathbb{M}_i}$ because $\delta \mathbb{E}_T$ is zero (since $\mathbb{E}_T$ is a minimum), $\delta \mathbb{S}_T$ is zero (since $\mathbb{S}_T$ is a maximum), and $\delta \mathbb{M}_{iT}$ is zero for all species i (since no reactions occur at equilibrium that would cause a change in mass of a chemical species). Thus the determination of conditions for equilibrium has been expressed as the determination of the conditions for which

$$\delta \mathbb{F}_T = 0 \, . \tag{4.15}$$

Substitution of Eqs. (4.10)–(4.12) into Eq. (4.14) subject to the equilibrium constraint of Eq. (4.15) gives the equilibrium condition as

$$0 = \sum_{\alpha \in \mathfrak{I}} \left[\delta \int_{\Omega_\alpha} (E_\alpha + \Psi_\alpha) \,\mathrm{d}\mathfrak{r} - \lambda_{\mathbb{S}} \delta \int_{\Omega_\alpha} \eta_\alpha \,\mathrm{d}\mathfrak{r} - \sum_{i \in \mathfrak{I}_s} \lambda_{\mathbb{M}_i} \delta \int_{\Omega_\alpha} \rho_\alpha \omega_{i\alpha} \,\mathrm{d}\mathfrak{r} \right] \tag{4.16}$$

or

$$0 = \sum_{\alpha \in \mathfrak{I}} \delta \int_{\Omega_\alpha} \left(E_\alpha + \Psi_\alpha - \lambda_{\mathbb{S}} \eta_\alpha - \sum_{i \in \mathfrak{I}_s} \lambda_{\mathbb{M}_i} \rho_\alpha \omega_{i\alpha} \right) \mathrm{d}\mathfrak{r} \,. \tag{4.17}$$

We emphasize that the integrals appearing in Eq. (4.16) are over phases, interfaces, and common curves, depending upon the domain of entity α so that this equation is a variational expression that accounts for the system as a whole, which is composed of all of the entities in the index set $\mathfrak{I}$.

To use Eq. (4.17) to deduce equilibrium conditions, we must be able to relate the variations of integrals to integrals involving the variations of microscale quantities. In other words, we need to interchange the order of integration and variation. This interchange is different depending on whether the domain is a volume, interface, or common curve. Derivations of the theorems that facilitate this interchange may be found in Appendix A and the results appear, for convenience, in Table 4.2. Recall that variation at the external boundaries of the domain is not considered as we are concerned with internal conditions. Thus a variation of an integral over a phase is due to variation of the quantities in the integrand and to the variation of the boundary of the phase within the system. These boundaries coincide with interfaces and common curves. The equation for the variation of an integral over a phase is Eq. (A.53) in the table (and Appendix A). The contributions due to integrand variation and boundary variation are accounted for, respectively, as the two terms on the right side of the equation. The variation of an integral over an interface is comprised of variation of the quantities in the integrand and variation of the boundary of the interface coincident with a common curve. These effects are given, respectively, as the first and third terms on the right side of Eq. (A.64) in the table. In addition, an interface may deform without its boundary points varying, providing another contribution to the variation of an integral over an interface. This deformation is represented in the second integral on the right side of Eq. (A.64). The variation of an integral over a common curve is due to the variation of the integrand, deformation of the curve, and movement of common points at the end of pieces of the curve. These elements of the variation of the integral over a curve are accounted for, respectively, by the three terms on the right side of Eq. (A.84) derived in Appendix A and appearing in Table 4.2.

Examination of the entries in Table 4.2 shows that the forms of the variations are all similar and thus can be expressed in a single form given in Eq. (A.86),

$$\delta F_\alpha = \int\limits_{\Omega_\alpha} \overline{\delta}^{(n)} f_\alpha \,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha} f_\alpha \nabla^{(n)}\cdot\mathsf{I}_\alpha^{(n)}\cdot\delta\mathbf{x}_\alpha \,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_\alpha} f_\alpha \mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha} \,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{J}\,. \tag{4.18}$$

In this equation, $n = 3 - \dim\alpha$, and (n) is replaced by n primes to obtain the form for each entity. Additionally, when $n = 2$, the case of a common curve, the last integral in the equation is replaced by a summation. We can also infer the form for the variation of a common point property, and this is given in the table. This inference is based on the facts that $\mathsf{I}_\alpha''' = 0$ and a point has no boundary.

To obtain a general expression for the variational analysis of multiphase systems, we employ the three theorems in Table 4.2 in Eq. (4.17) by identifying the portions of the summation that are over phases, interfaces, and common curves. In the interest of keeping the equations short, the general form of Eq. (4.18) will be employed; explicit expansion for terms corresponding to the specific entities is postponed until later. Application of Eq. (4.18) to Eq. (4.17) yields

$$\begin{aligned}
0 = {} & \sum_{\alpha\in\mathfrak{J}} \int\limits_{\Omega_\alpha} \left[\overline{\delta}^{(n)} E_\alpha + \overline{\delta}^{(n)} \Psi_\alpha - \lambda_{\mathbb{S}} \overline{\delta}^{(n)} \eta_\alpha - \sum_{i\in\mathfrak{J}_s} \lambda_{\mathbb{M}_i} \overline{\delta}^{(n)} (\rho_\alpha \omega_{i\alpha}) \right] \mathrm{d}\mathfrak{r} \\
& - \sum_{\alpha\in\mathfrak{J}} \int\limits_{\Omega_\alpha} \left(E_\alpha + \Psi_\alpha - \lambda_{\mathbb{S}} \eta_\alpha - \sum_{i\in\mathfrak{J}_s} \lambda_{\mathbb{M}_i} \rho_\alpha \omega_{i\alpha} \right) (\nabla^{(n)}\cdot\mathsf{I}_\alpha^{(n)})\cdot\delta\mathbf{x}_\alpha \,\mathrm{d}\mathfrak{r} \\
& + \sum_{\alpha\in\mathfrak{J}} \int\limits_{\Gamma_\alpha} \left(E_\alpha + \Psi_\alpha - \lambda_{\mathbb{S}} \eta_\alpha - \sum_{i\in\mathfrak{J}_s} \lambda_{\mathbb{M}_i} \rho_\alpha \omega_{i\alpha} \right) \mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha} \,\mathrm{d}\mathfrak{r}\,,
\end{aligned} \tag{4.19}$$

where $n = 3 - \dim\alpha$ and integrals over points imply summations.

Next we will particularize Eq. (4.19) to a form that retains generality but is targeted at porous medium analysis with one phase being a solid (i.e., $\alpha = s$). Because the expression for energy of an elastic solid as given by Eq. (3.159) is different from that for a fluid, as in Eq. (3.156), it is useful to separate the summation over phases in Eq. (4.19) to a part that is over the fluid phases and a part over a solid phase. The index set of phases, $\mathfrak{J}_\mathrm{P}$, satisfies the relation $\mathfrak{J}_\mathrm{P} = \mathfrak{J}_\mathrm{f} \cup \mathfrak{J}_\mathrm{S}$ where $\mathfrak{J}_\mathrm{f}$ is the index set of fluid phases and $\mathfrak{J}_\mathrm{S}$ is the solid phase index set. In this instance, $\mathfrak{J}_\mathrm{S} = \{s\}$. For convenience, we will also make use of the notation $\mathfrak{J}_{/\mathrm{S}}$ to indicate the index set of all entities except the solid phase such that $\mathfrak{J} = \mathfrak{J}_\mathrm{S} \cup \mathfrak{J}_{/\mathrm{S}}$. Additionally, we will make use of the following information to re-express certain terms in the equation:

- CIT representations of microscopic energy densities for the fluid phase, the elastic solid, the interface, and the common curve are given by Eqs. (3.156), (3.159), (3.161), and (3.163) respectively. These definitions are used to eliminate the energy densities from Eq. (4.19).
- Common points will be considered to have no thermodynamic properties of their own. Rather they are simply junctions where common curves meet. Thus, in

any summations, quantities that would be properties of common points can be dropped (i.e., E_α, ρ_α, Ψ_α, and η_α are all zero for $\alpha \in \mathfrak{J}_{\mathrm{Pt}}$).

- The variations $\overline{\delta}^{(n)} E_\alpha$ for $\alpha \in \mathfrak{J}$ are eliminated from Eq. (4.19) using equalities in Table 4.1.
- Use is made of the identity $\Psi_\alpha = \sum\limits_{i\in\mathfrak{J}_s} \rho_\alpha \omega_{i\alpha} \psi_{i\alpha}$ for $\alpha \in \mathfrak{J}$.
- The identities involving variations of gravity potentials in Table 4.1 are used in the equation with $\overline{\delta}^{(n)} \psi_{i\alpha} = -\mathbf{g}_{i\alpha} \cdot (\mathsf{I} - \mathsf{l}_\alpha^{(n)}) \cdot \delta \mathbf{x}_\alpha$.

Incorporating the changes annotated above into Eq. (4.19) yields

$$\begin{aligned}
0 = & \sum_{\alpha\in\mathfrak{J}} \int\limits_{\Omega_\alpha} \left[(\theta_\alpha - \lambda_{\mathbb{S}}) \overline{\delta}^{(n)} \eta_\alpha + \sum_{i\in\mathfrak{J}_s} \left(\mu_{i\alpha} + \psi_{i\alpha} - \lambda_{\mathbb{M}_i}\right) \overline{\delta}^{(n)} (\rho_\alpha \omega_{i\alpha}) \right] \mathrm{d}\mathfrak{r} \\
& + \sum_{\alpha\in\mathfrak{J}} \int\limits_{\Gamma_\alpha} \left[(\theta_\alpha - \lambda_{\mathbb{S}}) \eta_\alpha + \sum_{i\in\mathfrak{J}_s} \left(\mu_{i\alpha} + \psi_{i\alpha} - \lambda_{\mathbb{M}_i}\right) \rho_\alpha \omega_{i\alpha} \right] \mathbf{n}_\alpha \cdot \delta \mathbf{x}_{\alpha\alpha} \, \mathrm{d}\mathfrak{r} \\
& - \sum_{\alpha\in\mathfrak{J}} \int\limits_{\Omega_\alpha} \left[(\theta_\alpha - \lambda_{\mathbb{S}}) \eta_\alpha + \sum_{i\in\mathfrak{J}_s} \left(\mu_{i\alpha} + \psi_{i\alpha} - \lambda_{\mathbb{M}_i}\right) \rho_\alpha \omega_{i\alpha} \right] (\nabla^{(n)} \cdot \mathsf{l}_\alpha^{(n)}) \cdot \delta \mathbf{x}_\alpha \, \mathrm{d}\mathfrak{r} \\
& - \sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}} \int\limits_{\Omega_\alpha} \gamma_\alpha (\nabla' \cdot \mathsf{l}'_\alpha) \cdot \delta \mathbf{x}_\alpha \, \mathrm{d}\mathfrak{r} + \sum_{\alpha\in\mathfrak{J}_{\mathrm{C}}} \int\limits_{\Omega_\alpha} \gamma_\alpha (\nabla'' \cdot \mathsf{l}''_\alpha) \cdot \delta \mathbf{x}_\alpha \, \mathrm{d}\mathfrak{r} \\
& - \sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}} \int\limits_{\Gamma_\alpha} p_\alpha \mathbf{n}_\alpha \cdot \delta \mathbf{x}_{\alpha\alpha} \, \mathrm{d}\mathfrak{r} + \sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}} \int\limits_{\Gamma_\alpha} \gamma_\alpha \mathbf{n}_\alpha \cdot \delta \mathbf{x}_{\alpha\alpha} \, \mathrm{d}\mathfrak{r} - \sum_{\alpha\in\mathfrak{J}_{\mathrm{C}}} \int\limits_{\Gamma_\alpha} \gamma_\alpha \mathbf{n}_\alpha \cdot \delta \mathbf{x}_{\alpha\alpha} \, \mathrm{d}\mathfrak{r} \\
& - \sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}} \int\limits_{\Omega_\alpha} \rho_\alpha \mathbf{g}_\alpha \cdot \left(\mathsf{I} - \mathsf{l}'_\alpha\right) \cdot \delta \mathbf{x}_\alpha \, \mathrm{d}\mathfrak{r} - \sum_{\alpha\in\mathfrak{J}_{\mathrm{C}}} \int\limits_{\Omega_\alpha} \rho_\alpha \mathbf{g}_\alpha \cdot \left(\mathsf{I} - \mathsf{l}''_\alpha\right) \cdot \delta \mathbf{x}_\alpha \, \mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Omega_s} \boldsymbol{\sigma}_s : \overline{\delta} \left(\frac{\mathsf{C}_s}{j_s} \right) \mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_s} \boldsymbol{\sigma}_s : \frac{\mathsf{C}_s}{j_s} \mathbf{n}_s \cdot \delta \mathbf{x}_{ss} \, \mathrm{d}\mathfrak{r} \, .
\end{aligned} \tag{4.20}$$

This equation consists of groups of terms multiplied by variations of microscopic quantities. However, the fixed-point variation of C_s / j_s is not independent of variations in $\mathbf{x}_s$. Therefore, prior to applying this equation to particular systems, it is necessary to further analyze this term.

4.4.1 Analysis of the Integral of $\boldsymbol{\sigma}_s : \overline{\delta}\left(\mathsf{C}_s / j_s\right)$

The term of interest is the next to the last term in Eq. (4.20), the integral over the solid domain. Apply the product rule to this term to obtain

$$\int_{\Omega_s} \boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right) \mathrm{d}\mathfrak{r} = -\int_{\Omega_s} \left[\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{j_s^2}\overline{\delta} j_s - \frac{1}{j_s}\boldsymbol{\sigma}_s{:}\overline{\delta}\mathbf{C}_s\right] \mathrm{d}\mathfrak{r} \,. \tag{4.21}$$

Make use of the expressions for δj_α and $\delta\rho_\alpha$ in Table 4.1 (or the fact that $\rho_s j_s$ is, by definition, constant) to show that

$$\overline{\delta} j_s = -\frac{j_s}{\rho_s}\overline{\delta}\rho_s \,. \tag{4.22}$$

Thus Eq. (4.21) becomes

$$\int_{\Omega_s} \boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right) \mathrm{d}\mathfrak{r} = \int_{\Omega_s} \left(\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\rho_s j_s}\overline{\delta}\rho_s + \frac{1}{j_s}\boldsymbol{\sigma}_s{:}\overline{\delta}\mathbf{C}_s\right) \mathrm{d}\mathfrak{r} \,. \tag{4.23}$$

Table 4.1 provides an identity for $\overline{\delta}\mathbf{C}_s$ so that we can further manipulate this equation to

$$\begin{aligned}\int_{\Omega_s} \boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right) \mathrm{d}\mathfrak{r} &= \int_{\Omega_s} \left(\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\rho_s j_s}\overline{\delta}\rho_s\right) \mathrm{d}\mathfrak{r} \\ &+ \int_{\Omega_s} \left\{\frac{2}{j_s}\left[(\nabla_X \mathbf{x}_s)^{\mathrm{T}}\cdot\boldsymbol{\sigma}_s\cdot\nabla_X\mathbf{x}_s\right]{:}\frac{1}{2}\left[\nabla(\delta\mathbf{x}_s) + [\nabla(\delta\mathbf{x}_s)]^{\mathrm{T}}\right]\right\} \mathrm{d}\mathfrak{r} \,.\end{aligned} \tag{4.24}$$

We identify the solid phase stress tensor, $\mathbf{t}_s$, as

$$\mathbf{t}_s = \frac{2}{j_s}(\nabla_X \mathbf{x}_s)^{\mathrm{T}}\cdot\boldsymbol{\sigma}_s\cdot\nabla_X\mathbf{x}_s \,. \tag{4.25}$$

Because $\mathbf{t}_s$ is symmetric, its insertion into Eq. (4.24) yields

$$\int_{\Omega_s} \boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right) \mathrm{d}\mathfrak{r} = \int_{\Omega_s} \left[\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\rho_s j_s}\overline{\delta}\rho_s + \mathbf{t}_s{:}\nabla(\delta\mathbf{x}_s)\right] \mathrm{d}\mathfrak{r} \,. \tag{4.26}$$

This last equation may be modified by writing it in terms of the deviatoric stress tensor, $\mathbf{t}_{s\mathrm{D}}$, where

$$\mathbf{t}_{s\mathrm{D}} = \mathbf{t}_s - \frac{\mathbf{t}_s{:}\mathbf{I}}{3}\mathbf{I} \,. \tag{4.27}$$

This change gives

$$\int_{\Omega_s} \boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right) \mathrm{d}\mathfrak{r} = \int_{\Omega_s} \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\rho_s j_s}\overline{\delta}\rho_s \,\mathrm{d}\mathfrak{r} + \int_{\Omega_s} \left[\mathbf{t}_{s\mathrm{D}}{:}\nabla(\delta\mathbf{x}_s) + \frac{\mathbf{t}_s{:}\mathbf{I}}{3}\nabla\cdot(\delta\mathbf{x}_s)\right] \mathrm{d}\mathfrak{r} \,. \tag{4.28}$$

Making use of the relation between the total and fixed point variations and the expression for $\delta\rho_\alpha$ in Table 4.1, we can show that

$$\nabla\cdot(\delta\mathbf{x}_s) = -\frac{1}{\rho_s}\overline{\delta}\rho_s - \frac{1}{\rho_s}(\delta\mathbf{x}_s)\cdot\nabla\rho_s\,. \tag{4.29}$$

We use this expression to eliminate $\nabla\cdot(\delta\mathbf{x}_s)$ from Eq. (4.28) and obtain, after rearrangement,

$$\begin{aligned}\int\limits_{\Omega_s}\boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right)\mathrm{d}\mathfrak{r} = &\int\limits_{\Omega_s}\left[\mathbf{t}_{s\mathrm{D}}{:}\nabla(\delta\mathbf{x}_s) - \left(\frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\nabla\rho_s\right)\cdot\delta\mathbf{x}_s\right]\mathrm{d}\mathfrak{r}\\ &+\int\limits_{\Omega_s}\left(\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\rho_s j_s} - \frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\right)\overline{\delta}\rho_s\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{4.30}$$

Apply the product rule and the divergence theorem to the first term so that the equation becomes

$$\begin{aligned}\int\limits_{\Omega_s}\boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right)\mathrm{d}\mathfrak{r} = &-\int\limits_{\Omega_s}\left(\nabla\cdot\mathbf{t}_{s\mathrm{D}} + \frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\nabla\rho_s\right)\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\\ &+\int\limits_{\Omega_s}\left(\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\rho_s j_s} - \frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\right)\overline{\delta}\rho_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_s}\mathbf{n}_s\cdot\mathbf{t}_{s\mathrm{D}}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{4.31}$$

It will prove convenient to revert back to the full stress tensor from the deviatoric tensor by using Eq. (4.27). Then after minor rearrangement, we obtain

$$\begin{aligned}\int\limits_{\Omega_s}\boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right)\mathrm{d}\mathfrak{r} = &-\int\limits_{\Omega_s}\left[\nabla\cdot\mathbf{t}_s - \rho_s\nabla\left(\frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\right)\right]\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_s}\left(\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\rho_s j_s} - \frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\right)\overline{\delta}\rho_s\,\mathrm{d}\mathfrak{r}\\ &+\int\limits_{\Gamma_s}\mathbf{n}_s\cdot\mathbf{t}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} - \int\limits_{\Gamma_s}\frac{\mathbf{t}_s{:}\mathbf{I}}{3}\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{4.32}$$

With $\mathbf{t}_s$ defined as in Eq. (4.25), we use the fact that

$$\mathbf{t}_s{:}\mathbf{I} = 2\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{j_s} \tag{4.33}$$

to further simplify Eq. (4.32) to

$$\begin{aligned}\int\limits_{\Omega_s}\boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right)\mathrm{d}\mathfrak{r} = &-\int\limits_{\Omega_s}\left[\nabla\cdot\mathbf{t}_s - \rho_s\nabla\left(\frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\right)\right]\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\\ +\int\limits_{\Omega_s}\left(\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3\rho_s j_s}\right)\overline{\delta}\rho_s\,\mathrm{d}\mathfrak{r} &+ \int\limits_{\Gamma_s}\mathbf{n}_s\cdot\mathbf{t}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} - \int\limits_{\Gamma_s}\frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{4.34}$$

As a last step in anticipating future utility of this expression, it will prove convenient to make use of the fact that the unit tensor, $\mathbf{I}$, can be decomposed according to

$\mathbf{I} = \mathbf{I}'_{ss} + \mathbf{n}_s\mathbf{n}_s$ on Γ_s such that

$$\int\limits_{\Gamma_s} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} = \int\limits_{\Gamma_s} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_s} (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)\,\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,. \tag{4.35}$$

Thus, Eq. (4.34) becomes

$$\begin{aligned}\int\limits_{\Omega_s} \boldsymbol{\sigma}_s{:}\overline{\delta}\left(\frac{\mathbf{C}_s}{j_s}\right)\mathrm{d}\mathfrak{r} = &-\int\limits_{\Omega_s}\left[\nabla\cdot\mathbf{t}_s - \rho_s\nabla\left(\frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\right)\right]\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_s}\left(\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3\rho_s j_s}\right)\overline{\delta}\rho_s\,\mathrm{d}\mathfrak{r}\\ &-\int\limits_{\Gamma_s}\frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_s}\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_s}(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)\,\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{4.36}$$

There is one particular feature of this equation that deserves mention. The integrands of the integrals over Γ_s contain $\delta\mathbf{x}_s$ rather than $\delta\mathbf{x}_{ss}$. This is a variation in the position vector of a solid phase coordinate. It is different from the variation of the position vector of the boundary of the solid phase. These two variations can be different if solid material is transferring into the interface. In all the integrals over Γ_α in Eq. (4.20), $\delta\mathbf{x}_{\alpha\alpha}$ is the variation of the coordinate on the boundary of entity α. This distinction is important in subsequent equations.

This completes the mathematical analysis of this subsection. Equation (4.36) will be used in conjunction with Eq. (4.20) to obtain the variational form for analyzing equilibrium of a multiphase system. The analysis of this section will not have to be repeated for the various specific systems of interest.

4.4.2 General Condition of Equilibrium

The preceding subsection is provided so that the mathematical derivation of the condition for equilibrium will be complete. If one is only interested in the result, then Eq. (4.36) can be taken on faith and substituted into Eq. (4.20) to continue the derivation of the physically important restriction. If we make this substitution and rearrange terms we obtain

$$\begin{aligned}0 = &\sum_{\alpha\in\mathfrak{J}}\int\limits_{\Omega_\alpha}(\theta_\alpha - \lambda_{\mathbb{S}})\,\overline{\delta}^{(n)}\eta_\alpha\,\mathrm{d}\mathfrak{r} + \sum_{\alpha\in\mathfrak{J}}\int\limits_{\Gamma_\alpha}(\theta_\alpha - \lambda_{\mathbb{S}})\,\eta_\alpha\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha}\,\mathrm{d}\mathfrak{r}\\ &-\sum_{\alpha\in\mathfrak{J}}\int\limits_{\Omega_\alpha}(\theta_\alpha - \lambda_{\mathbb{S}})\,\eta_\alpha(\nabla^{(n)}\cdot\mathbf{I}^{(n)}_\alpha)\cdot\delta\mathbf{x}_\alpha\,\mathrm{d}\mathfrak{r}\\ &+\sum_{\alpha\in\mathfrak{J}_{/\mathrm{S}}}\sum_{i\in\mathfrak{J}_s}\int\limits_{\Omega_\alpha}\left(\mu_{i\alpha} + \psi_{i\alpha} - \lambda_{\mathbb{M}_i}\right)\overline{\delta}^{(n)}(\rho_\alpha\omega_{i\alpha})\,\mathrm{d}\mathfrak{r}\end{aligned}$$

$$
\begin{aligned}
&+\sum_{\alpha\in\mathfrak{J}_{/\mathrm{S}}}\sum_{i\in\mathfrak{J}_s}\int_{\Gamma_\alpha}\left(\mu_{i\alpha}+\psi_{i\alpha}-\lambda_{\mathbb{M}_i}\right)\rho_\alpha\omega_{i\alpha}\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha}\,\mathrm{d}\mathfrak{r}\\
&-\sum_{\alpha\in\mathfrak{J}_{/\mathrm{S}}}\sum_{i\in\mathfrak{J}_s}\int_{\Omega_\alpha}\left(\mu_{i\alpha}+\psi_{i\alpha}-\lambda_{\mathbb{M}_i}\right)\rho_\alpha\omega_{i\alpha}(\nabla^{(n)}\cdot\mathsf{l}_\alpha^{(n)})\cdot\delta\mathbf{x}_\alpha\,\mathrm{d}\mathfrak{r}\\
&+\sum_{i\in\mathfrak{J}_s}\int_{\Omega_s}\left(\mu_{is}+\psi_{is}+\frac{\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s\rho_s}-\lambda_{\mathbb{M}_i}\right)\overline{\delta}(\rho_s\omega_{is})\,\mathrm{d}\mathfrak{r}\\
&+\sum_{i\in\mathfrak{J}_s}\int_{\Gamma_s}\left(\mu_{is}+\psi_{is}+\frac{\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{\rho_s j_s}-\lambda_{\mathbb{M}_i}\right)\rho_s\omega_{is}\mathbf{n}_s\cdot\delta\mathbf{x}_{ss}\,\mathrm{d}\mathfrak{r}\\
&-\sum_{\alpha\in\mathfrak{J}_\mathrm{I}}\int_{\Omega_\alpha}\gamma_\alpha(\nabla'\cdot\mathsf{l}'_\alpha)\cdot\delta\mathbf{x}_\alpha\,\mathrm{d}\mathfrak{r}+\sum_{\alpha\in\mathfrak{J}_\mathrm{C}}\int_{\Omega_\alpha}\gamma_\alpha(\nabla''\cdot\mathsf{l}''_\alpha)\cdot\delta\mathbf{x}_\alpha\,\mathrm{d}\mathfrak{r}\\
&-\sum_{\alpha\in\mathfrak{J}_\mathrm{f}}\int_{\Gamma_\alpha}p_\alpha\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha}\,\mathrm{d}\mathfrak{r}+\sum_{\alpha\in\mathfrak{J}_\mathrm{I}}\int_{\Gamma_\alpha}\gamma_\alpha\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha}\,\mathrm{d}\mathfrak{r}-\sum_{\alpha\in\mathfrak{J}_\mathrm{C}}\int_{\Gamma_\alpha}\gamma_\alpha\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha}\,\mathrm{d}\mathfrak{r}\\
&-\sum_{\alpha\in\mathfrak{J}_\mathrm{I}}\int_{\Omega_\alpha}\rho_\alpha\mathbf{g}_\alpha\cdot\left(\mathsf{l}-\mathsf{l}'_\alpha\right)\cdot\delta\mathbf{x}_\alpha\,\mathrm{d}\mathfrak{r}-\sum_{\alpha\in\mathfrak{J}_\mathrm{C}}\int_{\Omega_\alpha}\rho_\alpha\mathbf{g}_\alpha\cdot\left(\mathsf{l}-\mathsf{l}''_\alpha\right)\cdot\delta\mathbf{x}_\alpha\,\mathrm{d}\mathfrak{r}\\
&-\int_{\Omega_s}\left[\nabla\cdot\mathbf{t}_s-\rho_s\nabla\left(\frac{\mathbf{t}_s{:}\mathsf{l}}{3\rho_s}\right)\right]\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\\
&+\int_{\Gamma_s}\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathsf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}+\int_{\Gamma_s}\left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s-\frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,. \qquad (4.37)
\end{aligned}
$$

The motivation for the preceding algebraic manipulations was to group terms that multiplied a common variational term integrated over the same domain. Since the independent variations are arbitrary, equilibrium will hold only if the multipliers of independent variations are zero. This stipulation will be examined further in the next sections in the context of two particular systems of interest: a porous medium system with a single fluid phase and a porous medium system with two fluid phases. Equation (4.37) will be employed as the starting point in the development of equilibrium conditions for these systems.

4.5 Single-fluid-phase Porous Medium System

A single-fluid-phase porous medium system consists of a fluid phase, designated as the *w* entity, a solid phase, designated as the *s* entity, and the interface between the phases, denoted as the *ws* entity. Thus, the index set for the phases, $\mathfrak{J}_\mathrm{P}$, is

$$\mathfrak{J}_\mathrm{P}=\{w,s\} \qquad (4.38)$$

and the index set for the interface, $\mathfrak{I}_{\mathrm{I}}$, is

$$\mathfrak{I}_{\mathrm{I}} = \{ws\} \,. \tag{4.39}$$

Since there are no common curves or common points for a two-phase system, the index sets for common curves, $\mathfrak{I}_{\mathrm{C}}$, and for common points, $\mathfrak{I}_{\mathrm{Pt}}$, are the null set, indicated as

$$\mathfrak{I}_{\mathrm{C}} = \{\varnothing\} \tag{4.40}$$

and

$$\mathfrak{I}_{\mathrm{Pt}} = \{\varnothing\} \,. \tag{4.41}$$

The index set for the entire system is denoted as $\mathfrak{I}$ and is defined as

$$\mathfrak{I} = \mathfrak{I}_{\mathrm{P}} \cup \mathfrak{I}_{\mathrm{I}} = \{w, s, ws\} \,. \tag{4.42}$$

The only fluid phase is the w phase and therefore the index set of fluids, $\mathfrak{I}_{\mathrm{f}}$, is

$$\mathfrak{I}_{\mathrm{f}} = \{w\} \,. \tag{4.43}$$

With this selection of indices to designate the phases and interfaces, Eq. (4.37) may be written in the form particular to the system of interest. There are no integrals/summations over common curves/points, and there is no boundary of the interface. Identities on the ws interface that apply for this two phase system are

$$\mathbf{n}_w \mathbf{n}_w = \mathsf{I} - \mathsf{I}'_{ws} \tag{4.44}$$

and

$$(\nabla' \cdot \mathbf{n}_w)\mathbf{n}_w = -\nabla' \cdot \mathsf{I}'_{ws} \,. \tag{4.45}$$

Because the variation of the boundary of a phase in the normal direction is equal to the variation of the boundary entity coordinate in the normal direction, the variation $\delta\mathbf{x}_{\alpha\alpha}$ can be expressed according to

$$\mathbf{n}_\alpha \cdot \delta\mathbf{x}_{\alpha\alpha} = \mathbf{n}_\alpha \cdot \delta\mathbf{x}_{ws} \text{ in integrals over } \Gamma_\alpha \text{ for } \alpha \in \mathfrak{I}_{\mathrm{P}} \,. \tag{4.46}$$

The resulting simplification of Eq. (4.37) for a single-fluid-phase porous medium is thus

$$\begin{aligned}
0 = & \sum_{\alpha \in \mathfrak{I}} \int_{\Omega_\alpha} (\theta_\alpha - \lambda_{\mathbb{S}}) \overline{\delta}^{(n)} \eta_\alpha \, \mathrm{d}\mathfrak{r} + \sum_{\alpha \in \mathfrak{I}_{\mathrm{P}}} \int_{\Gamma_\alpha} (\theta_\alpha - \lambda_{\mathbb{S}}) \, \eta_\alpha \mathbf{n}_\alpha \cdot \delta\mathbf{x}_{ws} \, \mathrm{d}\mathfrak{r} \\
& + \int_{\Omega_{ws}} (\theta_{ws} - \lambda_{\mathbb{S}}) \, \eta_{ws} (\nabla' \cdot \mathbf{n}_w) \mathbf{n}_w \cdot \delta\mathbf{x}_{ws} \, \mathrm{d}\mathfrak{r} \\
& + \sum_{\alpha \in \mathfrak{I}_{/\mathrm{S}}} \sum_{i \in \mathfrak{I}_s} \int_{\Omega_\alpha} \left(\mu_{i\alpha} + \psi_{i\alpha} - \lambda_{\mathbb{M}_i} \right) \overline{\delta}^{(n)} (\rho_\alpha \omega_{i\alpha}) \, \mathrm{d}\mathfrak{r}
\end{aligned}$$

$$
\begin{aligned}
&+\sum_{i\in\mathfrak{I}_s}\int\limits_{\Gamma_w}\left(\mu_{iw}+\psi_{iw}-\lambda_{\mathbb{M}_i}\right)\rho_w\omega_{iw}\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&+\sum_{i\in\mathfrak{I}_s}\int\limits_{\Omega_{ws}}\left(\mu_{iws}+\psi_{iws}-\lambda_{\mathbb{M}_i}\right)\rho_{ws}\omega_{iws}(\nabla'\cdot\mathbf{n}_w)\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&+\sum_{i\in\mathfrak{I}_s}\int\limits_{\Omega_s}\left(\mu_{is}+\psi_{is}+\frac{\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s\rho_s}-\lambda_{\mathbb{M}_i}\right)\overline{\delta}(\rho_s\omega_{is})\,\mathrm{d}\mathfrak{r}\\
&+\sum_{i\in\mathfrak{I}_s}\int\limits_{\Gamma_s}\left(\mu_{is}+\psi_{is}+\frac{\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{\rho_s j_s}-\lambda_{\mathbb{M}_i}\right)\rho_s\omega_{is}\mathbf{n}_s\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&+\int\limits_{\Omega_{ws}}\left[\gamma_{ws}(\nabla'\cdot\mathbf{n}_w)-\rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_w\right]\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}-\int\limits_{\Gamma_w}p_w\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&-\int\limits_{\Omega_s}\left[\nabla\cdot\mathsf{t}_s-\rho_s\nabla\left(\frac{\mathsf{t}_s{:}\mathsf{I}}{3\rho_s}\right)\right]\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\\
&+\int\limits_{\Gamma_s}\mathbf{n}_s\cdot\mathsf{t}_s\cdot\mathsf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}+\int\limits_{\Gamma_s}\left(\mathbf{n}_s\cdot\mathsf{t}_s\cdot\mathbf{n}_s-\frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,.
\end{aligned}
\tag{4.47}
$$

To arrange Eq. (4.47) to a form that provides equilibrium conditions, we have to express it in terms of independent variations. Therefore, we make the following observations and substitutions:

- The boundaries of the w and s phases are the ws interface. Therefore, integrals over Γ_s and Γ_w may be changed to integrals over Ω_{ws} when convenient; and l'_{ss} may be replaced by l'_{ws}.
- Because $\mathbf{n}_s = -\mathbf{n}_w$ on Ω_{ws}, $\mathbf{n}_s$ may be eliminated from Eq. (4.47) when desired.

Use of this information in Eq. (4.47), followed by rearrangement and grouping of terms in the resultant expression, yields

$$
\begin{aligned}
0=&\sum_{\alpha\in\mathfrak{I}}\int\limits_{\Omega_\alpha}(\theta_\alpha-\lambda_{\mathbb{S}})\overline{\delta}^{(n)}\eta_\alpha\,\mathrm{d}\mathfrak{r}+\sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\int\limits_{\Gamma_\alpha}(\theta_\alpha-\lambda_{\mathbb{S}})\eta_\alpha\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&+\int\limits_{\Omega_{ws}}(\theta_{ws}-\lambda_{\mathbb{S}})\eta_{ws}(\nabla'\cdot\mathbf{n}_w)\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&+\sum_{\alpha\in\mathfrak{I}_{/\mathrm{S}}}\sum_{i\in\mathfrak{I}_s}\int\limits_{\Omega_\alpha}\left(\mu_{i\alpha}+\psi_{i\alpha}-\lambda_{\mathbb{M}_i}\right)\overline{\delta}^{(n)}(\rho_\alpha\omega_{i\alpha})\,\mathrm{d}\mathfrak{r}\\
&+\sum_{i\in\mathfrak{I}_s}\int\limits_{\Gamma_w}\left(\mu_{iw}+\psi_{iw}-\lambda_{\mathbb{M}_i}\right)\rho_w\omega_{iw}\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}
\end{aligned}
$$

$$\begin{aligned}
&+\sum_{i\in\mathfrak{I}_s}\int_{\Omega_{ws}}\left(\mu_{iws}+\psi_{iws}-\lambda_{\mathbb{M}_i}\right)\rho_{ws}\omega_{iws}(\nabla'\cdot\mathbf{n}_w)\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&+\sum_{i\in\mathfrak{I}_s}\int_{\Omega_s}\left(\mu_{is}+\psi_{is}+\frac{\boldsymbol{\sigma}_s{:}\mathsf{\mathbf{C}}_s}{3\rho_s j_s}-\lambda_{\mathbb{M}_i}\right)\overline{\delta}(\rho_s\omega_{is})\,\mathrm{d}\mathfrak{r}\\
&+\sum_{i\in\mathfrak{I}_s}\int_{\Gamma_s}\left(\mu_{is}+\psi_{is}+\frac{\boldsymbol{\sigma}_s{:}\mathsf{\mathbf{C}}_s}{3\rho_s j_s}-\lambda_{\mathbb{M}_i}\right)\rho_s\omega_{is}\mathbf{n}_s\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&-\int_{\Omega_s}\left[\nabla\cdot\mathsf{\mathbf{t}}_s-\rho_s\nabla\left(\frac{\mathsf{\mathbf{t}}_s{:}\mathsf{\mathbf{I}}}{3\rho_s}\right)\right]\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\\
&+\int_{\Omega_{ws}}\left[\gamma_{ws}(\nabla'\cdot\mathbf{n}_w)-\rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_w-p_w-\frac{2\boldsymbol{\sigma}_s{:}\mathsf{\mathbf{C}}_s}{3j_s}\right]\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r}\\
&+\int_{\Omega_{ws}}\mathbf{n}_s\cdot\mathsf{\mathbf{t}}_s\cdot\mathsf{\mathbf{I}}'_{ws}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}+\int_{\Omega_{ws}}\left(\mathbf{n}_s\cdot\mathsf{\mathbf{t}}_s\cdot\mathbf{n}_s-\frac{2\boldsymbol{\sigma}_s{:}\mathsf{\mathbf{C}}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,. \qquad (4.48)
\end{aligned}$$

The equilibrium conditions can be determined directly by requiring that each of the coefficients of independent variations be zero. This also serves to determine the values of the constant Lagrange multipliers, $\lambda_{\mathbb{S}}$ and $\lambda_{\mathbb{M}_i}$. These equilibrium conditions will be stated explicitly in the next subsection.

4.5.1 Equilibrium Conditions

The coefficients of each of the variations of entropy, $\overline{\delta}\eta_w$, $\overline{\delta}\eta_s$, and $\overline{\delta}'\eta_{ws}$, must be zero. Thus,

$$\theta_w=\theta_s=\theta_{ws}=\lambda_{\mathbb{S}}\,, \qquad (4.49)$$

which means that the equilibrium temperatures of all entities are equal to each other and constant, since $\lambda_{\mathbb{S}}$ is a constant. Additionally, the coefficients of each of the variations of the mass density of each chemical species in each entity must be zero such that

$$\mu_{iw}+\psi_{iw}=\mu_{is}+\psi_{is}+\frac{\boldsymbol{\sigma}_s{:}\mathsf{\mathbf{C}}_s}{3\rho_s j_s}=\mu_{iws}+\psi_{iws}=\lambda_{\mathbb{M}_i}\quad\text{for } i\in\mathfrak{I}_s\,. \qquad (4.50)$$

This condition specifies that for each chemical species, the sum of its chemical plus gravitational potentials will be constant and equal for a species in the fluid phase or the interface. Note that this sum of potentials for one species is not equal to that for another species. In extending the equality to include species in the solid phase, the additional term must be included that accounts for the deformation of the solid phase. The equilibration of temperatures and of potentials presumes that heat and mass, respectively, may be exchanged between entities. If these cannot be transferred between entities, one can show that the equilibrium condition is simply that the quantities indicated must still be constant but may take on different values in different entities. The requirements of Eqs. (4.49) and (4.50) ensure that the first eight integrals in Eq. (4.48) will be zero. We now turn to the last four integrals in this equation.

The variations in each of the last four integrals are independent because they are involved with different integration domains or in different directions on the boundary. The variations in the direction normal to the *ws* interface, $-\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}$ and $\mathbf{n}_s\cdot\delta\mathbf{x}_s$, will only be equal if there is no mass change occurring. Thus, these are independent variations at the boundary. The requirement that each coefficient of the independent variations must be zero at equilibrium gives four additional conditions of equilibrium:

$$\nabla\cdot\mathbf{t}_s - \rho_s\nabla\left(\frac{\mathbf{t}_s:\mathbf{I}}{3\rho_s}\right) = \mathbf{0} \quad \text{for } \mathbf{x}\in\Omega_s\,, \tag{4.51}$$

$$p_w + \frac{2\boldsymbol{\sigma}_s:\mathbf{C}_s}{3j_s\rho_s} - (\nabla\cdot\mathbf{n}_w)\,\gamma_{ws} + \rho_{ws}\mathbf{n}_w\cdot\mathbf{g}_{ws} = 0 \quad \text{for } \mathbf{x}\in\Omega_{ws}\,, \tag{4.52}$$

$$\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s:\mathbf{C}_s}{3j_s} = 0 \quad \text{for } \mathbf{x}\in\Omega_{ws}\,, \tag{4.53}$$

and

$$\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws} = \mathbf{0}' \quad \text{for } \mathbf{x}\in\Omega_{ws}\,. \tag{4.54}$$

Equation (4.51) is consistent with the equilibrium condition satisfied by conservation of momentum Eq. (2.27), as can be proven as an exercise; it adds no information beyond what the momentum equation provides. Equation (4.52) states that the normal forces exerted at the interface by the *w* and *s* phases are balanced by gravitational effects associated with the mass per area of the interface and the interfacial tension on a curved interface. For convenience, combine Eqs. (4.52) and (4.53) to provide the alternative, and perhaps more intuitive, equilibrium relation,

$$p_w + \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - (\nabla\cdot\mathbf{n}_w)\,\gamma_{ws} + \rho_{ws}\mathbf{n}_w\cdot\mathbf{g}_{ws} = 0 \quad \text{for } \mathbf{x}\in\Omega_{ws}\,. \tag{4.55}$$

This equation is an extension of the Young-Laplace equation [5, 13, 19] that describes capillary forces between fluids. Here, the condition applies to an interface between a fluid and a solid and also takes into account the possibility of the mass per area of the interface being non-zero. When the interface is massless and flat, the last two terms on the left side of Eq. (4.55) will be zero such that the normal forces exerted by the phases are equal at equilibrium.

4.6 Two-fluid-phase Porous Medium System

As a second example application of the use of variational methods to determine equilibrium conditions, we consider a two-fluid-phase porous medium system. The analysis is similar to that performed in Sect. 4.5 for a single-fluid porous medium, although somewhat more complicated because the physics of the system are more involved. Equation (4.37) serves as a useful starting point for the equilibrium analysis. Expansion of the summations over entities to the form needed to describe the three-phase system leads to a long equation. However, by careful identification of the appropriate index sets, we can dispose of some of the equilibrium conditions expeditiously and focus our effort on extraction of the equilibrium conditions that supplement those achieved for the simpler single-fluid-phase porous medium system.

4.6.1 *Identification of Index Sets*

The system of interest consists of a fluid phase, w, that preferentially wets the solid phase, s, and a second fluid phase, n, that is a non-wetting phase. For this system, there are three interface entities, denoted as wn, ws, and ns, that separate pairs of phases and serve as the boundaries of the phases. Additionally, a common curve entity denoted as wns is the boundary of an interface and is also the location where the three interfaces, as well as three phases, meet. For this type of porous medium system, the index set for the phases, $\mathcal{I}_{\mathrm{P}}$, is

$$\mathcal{I}_{\mathrm{P}} = \{w, n, s\} \; ; \tag{4.56}$$

the index set for the interfaces, $\mathcal{I}_{\mathrm{I}}$, is

$$\mathcal{I}_{\mathrm{I}} = \{wn, ws, ns\} \; ; \tag{4.57}$$

and the index set for the common curve, $\mathcal{I}_{\mathrm{C}}$, is

$$\mathcal{I}_{\mathrm{C}} = \{wns\} \; . \tag{4.58}$$

In the designation of interfaces and common curves, the order of the indices is irrelevant. This system has no common points, so the index set for the entire system, $\mathcal{I}$, is

$$\mathcal{I} = \mathcal{I}_{\mathrm{P}} \cup \mathcal{I}_{\mathrm{I}} \cup \mathcal{I}_{\mathrm{C}} = \{w, n, s, wn, ws, ns, wns\} \; . \tag{4.59}$$

Since there are two fluid phases, the index set for the fluids is $\mathcal{I}_{\mathrm{f}}$ where

$$\mathcal{I}_{\mathrm{f}} = \{w, n\} \; . \tag{4.60}$$

With these index sets, Eq. (4.37) may be applied directly to a two-fluid-phase porous medium system. We will make use of experience gained in the previous section to identify some of the equilibrium conditions rather than working with the fully expanded equation explicitly.

4.6.2 Identification of Simpler Equilibrium Conditions

Equilibrium conditions for multiphase systems should not contradict any conditions for single-phase or two-phase systems. They should be extensions of those conditions and should be consistent in trivial cases, such as when one phase has no properties and occupies no space. Based on this idea, we can immediately deduce the simpler equilibrium conditions for the two-fluid-phase porous medium system and then spend more effort on obtaining extensions.

The coefficients of independent variations in Eq. (4.37) must all be zero. Each of the fixed variations of entropy is independent of all other variations such that their coefficients must be zero. Therefore,

$$\theta_w = \theta_n = \theta_s = \theta_{wn} = \theta_{ws} = \theta_{ns} = \theta_{wns} = \lambda_{\mathbb{S}} \, . \tag{4.61}$$

The equalities provide the unsurprising condition that at equilibrium, the temperatures of all entities in thermal contact are equal and constant.

The variations of the mass densities of the chemical species are also independent such that their coefficients must be zero. This stipulation provides

$$\begin{aligned} \mu_{iw} + \psi_{iw} = \mu_{in} + \psi_{in} = \mu_{is} + \psi_{is} + \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3\rho_s j_s} = \mu_{iwn} + \psi_{iwn} \\ = \mu_{iws} + \psi_{iws} = \mu_{ins} + \psi_{ins} = \mu_{iwns} + \psi_{iwns} = \lambda_{\mathbb{M}_i} \quad \text{for } i \in \mathfrak{I}_s \, . \end{aligned} \tag{4.62}$$

This set of equalities states the conditions for which transfer of chemical species between entities does not occur. At equilibrium, the sum of chemical and gravitational potentials, plus an additional contribution for the solid phase deformation, for each chemical species will be equal in all entities and constant. Different species may take on different constant values.

The last simple condition is obtained by the observation that there is only one term associated with $\delta\mathbf{x}_s$ within the solid domain. This is the second to the last integral term in Eq. (4.37). Therefore, the coefficient of this variation must be zero so that, identically to Eq. (4.51) for the single- fluid phase case,

$$\nabla\cdot\mathbf{t}_s - \rho_s \nabla\left(\frac{\mathbf{t}_s{:}\mathbf{I}}{3\rho_s}\right) = \mathbf{0} \quad \text{for } \mathbf{x} \in \Omega_s \, . \tag{4.63}$$

This condition should not be surprising as one would expect that the condition of stress equilibrium within the solid phase should be independent of the number or distribution of fluid phases it contacts. On the other hand, equilibrium conditions at the boundary of the solid phase should depend on interactions with other entities.

The equilibrium conditions provided by Eqs. (4.61)–(4.63) allow for simplification of the variational equilibrium relation Eq. (4.37) applied to the two-fluid-phase system. In the next subsection, we will work with the remaining terms in that equation to obtain the additional conditions of equilibrium.

4.6.3 Equilibrium Variational Analysis

The identification of the simple equilibrium conditions in the last subsection allows many of the terms in Eq. (4.37) to be eliminated. The remaining part of the equation that must be examined, in light of the system entities, is

$$
\begin{aligned}
0 = {} & \int\limits_{\Gamma_s} \left(\frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right) \mathbf{n}_s\cdot\delta\mathbf{x}_{ss}\,\mathrm{d}\mathfrak{r} - \sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}} \int\limits_{\Omega_\alpha} \gamma_\alpha(\nabla'\cdot\mathsf{l}'_\alpha)\cdot\delta\mathbf{x}_\alpha\,\mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Omega_{wns}} \gamma_{wns}(\nabla''\cdot\mathsf{l}''_{wns})\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r} - \sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}} \int\limits_{\Gamma_\alpha} p_\alpha\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha}\,\mathrm{d}\mathfrak{r} + \sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}} \int\limits_{\Gamma_\alpha} \gamma_\alpha\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha}\,\mathrm{d}\mathfrak{r} \\
& - \sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}} \int\limits_{\Omega_\alpha} \rho_\alpha\mathbf{g}_\alpha\cdot\left(\mathsf{I}-\mathsf{l}'_\alpha\right)\cdot\delta\mathbf{x}_\alpha\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_{wns}} \rho_{wns}\mathbf{g}_{wns}\cdot\left(\mathsf{I}-\mathsf{l}''_{wns}\right)\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Gamma_s} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathsf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_s} \left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right) \mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,. \qquad (4.64)
\end{aligned}
$$

With use of the index sets identified in Sect. 4.6.1, the summations over entities may be expanded out. Additionally, we make use of equations for the tensor l'_α analogous to Eqs. (4.44) and (4.45) and also recognize that $\mathsf{l}''_{wns} = \mathbf{l}_{wns}\mathbf{l}_{wns}$. Thus we obtain

$$
\begin{aligned}
0 = {} & \int\limits_{\Gamma_s} \left(\frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right) \mathbf{n}_s\cdot\delta\mathbf{x}_{ss}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{wn}} (\nabla'\cdot\mathbf{n}_w)\gamma_{wn}\mathbf{n}_w\cdot\delta\mathbf{x}_{wn}\,\mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Omega_{ws}} (\nabla'\cdot\mathbf{n}_w)\gamma_{ws}\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} (\nabla'\cdot\mathbf{n}_n)\gamma_{ns}\mathbf{n}_n\cdot\delta\mathbf{x}_{ns}\,\mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Omega_{wns}} \gamma_{wns}\left(\mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\right)\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Gamma_w} p_w\mathbf{n}_w\cdot\delta\mathbf{x}_{ww}\,\mathrm{d}\mathfrak{r} \\
& - \int\limits_{\Gamma_n} p_n\mathbf{n}_n\cdot\delta\mathbf{x}_{nn}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{wn}} \gamma_{wn}\mathbf{n}_{wn}\cdot\delta\mathbf{x}_{wnwn}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{ws}} \gamma_{ws}\mathbf{n}_{ws}\cdot\delta\mathbf{x}_{wsws}\,\mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Gamma_{ns}} \gamma_{ns}\mathbf{n}_{ns}\cdot\delta\mathbf{x}_{nsns}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_{wn}} (\rho_{wn}\mathbf{g}_{wn}\cdot\mathbf{n}_w)\,\mathbf{n}_w\cdot\delta\mathbf{x}_{wn}\,\mathrm{d}\mathfrak{r} \\
& - \int\limits_{\Omega_{ws}} (\rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_w)\,\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_{ns}} (\rho_{ns}\mathbf{g}_{ns}\cdot\mathbf{n}_n)\,\mathbf{n}_n\cdot\delta\mathbf{x}_{ns}\,\mathrm{d}\mathfrak{r} \\
& - \int\limits_{\Omega_{wns}} \rho_{wns}\mathbf{g}_{wns}\cdot(\mathsf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns})\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_s} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathsf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}
\end{aligned}
$$

$$+\int_{\Gamma_s}\left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s-\frac{2\boldsymbol{\sigma}_s:\mathbf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,. \tag{4.65}$$

The objective now is to express all the integrals in the preceding equation that are over boundaries of entities as integrals over the domains of entities.

The domains of integration are related to one another in that interfaces are boundaries of phases, and the common curve is the boundary of the interfaces[1]. Because we are not considering concentrated forces from the fluid phases at the common curve, for the *w* phase we can change the integrals over the boundaries of the fluid phases to integrals over interface entities, noting that

$$\Gamma_w=\Omega_{ws}\cup\Omega_{wn}\,. \tag{4.66}$$

For the *n* phase, the corresponding equation is

$$\Gamma_n=\Omega_{wn}\cup\Omega_{ns}\,. \tag{4.67}$$

The normal component of the variation of a phase boundary is equal to the normal component of the variation of the entity that comprises the phase boundary. Therefore we obtain

$$\int_{\Gamma_w}p_w\mathbf{n}_w\cdot\delta\mathbf{x}_{ww}\,\mathrm{d}\mathfrak{r}=\int_{\Omega_{wn}}p_w\mathbf{n}_w\cdot\delta\mathbf{x}_{wn}\,\mathrm{d}\mathfrak{r}+\int_{\Omega_{ws}}p_w\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r} \tag{4.68}$$

and

$$\int_{\Gamma_n}p_n\mathbf{n}_n\cdot\delta\mathbf{x}_{nn}\,\mathrm{d}\mathfrak{r}=\int_{\Omega_{wn}}p_n\mathbf{n}_n\cdot\delta\mathbf{x}_{wn}\,\mathrm{d}\mathfrak{r}+\int_{\Omega_{ns}}p_n\mathbf{n}_n\cdot\delta\mathbf{x}_{ns}\,\mathrm{d}\mathfrak{r}\,. \tag{4.69}$$

These decompositions are directly implemented in the two-fluid pressure integrals of Eq. (4.65).

The solid phase boundary is treated slightly differently because we need to account for a concentrated stress that may act at the common curve. We will consider solids to satisfy the condition that $\mathbf{n}_s$ is unique at every point on the solid surface. However, the force exerted on the surface by the common curve may require the solid to deform or sustain a strain. Recall that the common curve is an idealization that has only a length dimension. The location where three phases come together is not actually a curve with no width but is a small region where properties change abruptly. The fact that fluids at equilibrium do not sustain a strain makes them different from solids, such that the decompositions of Eqs. (4.68) and (4.69) are useful for changing the domains of integration. At the smooth solid, we note that the solid stress may respond to the common curve forces such that

$$\mathbf{t}_s=\mathbf{t}_s^*\delta(\mathbf{x}-\mathbf{x}_{wns}), \tag{4.70}$$

---

[1] Recall that we are not considering the external boundary of the domain since all variations are specified to be zero at the boundaries.

where $\delta(\mathbf{x}-\mathbf{x}_{wns})$ is a Dirac delta function for a curve that acts on the surface at the coordinates of the common curve, $\mathbf{x}_{wns}$. Integration of the concentrated force at the common curve over a surface simplifies to an integral over the common curve with

$$\int\limits_{\Gamma_s} [\mathbf{n}_s\cdot\mathbf{t}_s^*\delta(\mathbf{x}-\mathbf{x}_{wns})\cdot\mathbf{n}_s]\,\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_{wns}} (\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s)\,\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} \tag{4.71}$$

and

$$\int\limits_{\Gamma_s} \mathbf{n}_s\cdot\mathbf{t}_s^*\delta(\mathbf{x}-\mathbf{x}_{wns})\cdot\mathbf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_{wns}} \mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,. \tag{4.72}$$

Thus integration of the solid stress contributions over Γ_s requires that the domain of the common curve, Ω_{wns}, as well as the domains of the fluid-solid interfaces, Ω_{ws} and Ω_{ns}, be considered. We obtain

$$\begin{aligned}\int\limits_{\Gamma_s} (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)\,\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} &= \int\limits_{\Omega_{ws}} (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)\,\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)\,\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\\ &\quad + \int\limits_{\Omega_{wns}} (\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s)\,\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\end{aligned} \tag{4.73}$$

and

$$\begin{aligned}\int\limits_{\Gamma_s} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} &= \int\limits_{\Omega_{ws}} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ns}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\\ &\quad + \int\limits_{\Omega_{wns}} \mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{4.74}$$

From similar reasoning, we obtain the equation

$$\begin{aligned}\int\limits_{\Gamma_s} \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} &= \int\limits_{\Omega_{ws}} \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\\ &\quad + \int\limits_{\Omega_{wns}} \frac{2\boldsymbol{\sigma}_s^*{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{4.75}$$

Also of interest is the first term on the right side of Eq. (4.65). The expression of this integral over Γ_s as an integral over Ω_{ws}, Ω_{ns}, and Ω_{wns} is similar to Eq. (4.75). However, one important difference is that the variation $\delta\mathbf{x}_{ss}$ must be converted to variations of the entity coordinates. With this in mind, we obtain

$$\int\limits_{\Gamma_s} \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_{ss}\,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_{ws}} \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_{ns}\,\mathrm{d}\mathfrak{r}$$

$$+ \int\limits_{\Omega_{wns}} \frac{2\boldsymbol{\sigma}_s^*{:}\mathsf{C}_s}{3j_s}\mathbf{n}_s\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r}\,. \tag{4.76}$$

Lastly, consider the three integrals of surface tension over the boundaries of the surface domain. For the two-fluid-phase system, there is only one common curve type, and this common curve is the boundary domain of all of the interfaces. The integrals of the surface tension have a common form, and the transformation to integrals over Ω_{wns} is written

$$\int\limits_{\Gamma_\alpha} \gamma_\alpha \mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\alpha}\,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_{wns}} \gamma_\alpha \mathbf{n}_\alpha\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I}\,. \tag{4.77}$$

Substitution of Eqs. (4.68) and (4.69) as well as Eqs. (4.73)–(4.77) into Eq. (4.65) eliminates all the integrals over entity boundaries in favor of integrals over entities. If the integrands for integrals over common domains are collected, Eq. (4.65) may be re-expressed as

$$\begin{aligned}
0 = &- \int\limits_{\Omega_{wn}} \left[p_w\mathbf{n}_w + p_n\mathbf{n}_n + (\rho_{wn}\mathbf{g}_{wn}\cdot\mathbf{n}_w)\,\mathbf{n}_w - (\nabla'\cdot\mathbf{n}_w)\gamma_{wn}\mathbf{n}_w\right]\cdot\delta\mathbf{x}_{wn}\,\mathrm{d}\mathfrak{r} \\
&- \int\limits_{\Omega_{ws}} \left[p_w\mathbf{n}_w - \left(\frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right)\mathbf{n}_s + (\rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_w)\,\mathbf{n}_w - (\nabla'\cdot\mathbf{n}_w)\gamma_{ws}\mathbf{n}_w\right]\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r} \\
&- \int\limits_{\Omega_{ns}} \left[p_n\mathbf{n}_n - \left(\frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right)\mathbf{n}_s + (\rho_{ns}\mathbf{g}_{ns}\cdot\mathbf{n}_n)\,\mathbf{n}_n - (\nabla'\cdot\mathbf{n}_n)\gamma_{ns}\mathbf{n}_n\right]\cdot\delta\mathbf{x}_{ns}\,\mathrm{d}\mathfrak{r} \\
&+ \int\limits_{\Omega_{ws}} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ns}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} \\
&+ \int\limits_{\Omega_{ws}} \left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} \left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s{:}\mathsf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} \\
&+ \int\limits_{\Omega_{wns}} \left(\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s^*{:}\mathsf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{wns}} \mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} \\
&+ \int\limits_{\Omega_{wns}} \left(\frac{2\boldsymbol{\sigma}_s^*{:}\mathsf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r} \\
&+ \int\limits_{\Omega_{wns}} \left[\gamma_{wn}\mathbf{n}_{wn} + \gamma_{ws}\mathbf{n}_{ws} + \gamma_{ns}\mathbf{n}_{ns} - \rho_{wns}\mathbf{g}_{wns}\cdot(\mathsf{I} - \mathbf{l}_{wns}\mathbf{l}_{wns})\right]\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r} \\
&+ \int\limits_{\Omega_{wns}} \gamma_{wns}\left(\mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\right)\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r}\,.
\end{aligned} \tag{4.78}$$

Further simplification can be achieved by making use of some equalities involving the normal vectors.

At the interface between phases, the normals to the respective phases are in opposite directions such that

$$\mathbf{n}_n = -\mathbf{n}_w \quad \text{for } \mathbf{x} \in \Omega_{wn} \; , \tag{4.79}$$

$$\mathbf{n}_s = -\mathbf{n}_w \quad \text{for } \mathbf{x} \in \Omega_{ws} \; , \tag{4.80}$$

and

$$\mathbf{n}_s = -\mathbf{n}_n \quad \text{for } \mathbf{x} \in \Omega_{ns} \; . \tag{4.81}$$

Because the solid surface is taken to be smooth such that it has a unique normal direction at every point, the normals at the common curve pointing outward from, and tangent to, the *ws* and *ns* interfaces will satisfy the condition that

$$\mathbf{n}_{ns} = -\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \; . \tag{4.82}$$

The unit vector $\mathbf{n}_{wn}$ at the common curve can be related to the normal and tangent to the surface according to

$$\mathbf{n}_{wn} = \cos\varphi_{ws,wn}\mathbf{n}_{ws} - \sin\varphi_{ws,wn}\mathbf{n}_s \quad \text{for } \mathbf{x} \in \Omega_{wns} \; , \tag{4.83}$$

where $\varphi_{ws,wn}$ is the angle between the *ws* and *wn* interfaces at the common curve.

Also, along the *wns* common curve the identity exists such that the curvature can be expressed as

$$\nabla''\cdot\mathbf{l}''_{wns} = \mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns} = \mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\cdot\mathbf{n}_s\mathbf{n}_s + \mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\cdot\mathbf{n}_{ws}\mathbf{n}_{ws} \; . \tag{4.84}$$

Then the normal curvature, κ_{Nwns}, and the geodesic curvature, κ_{Gwns}, are defined, respectively, as

$$\kappa_{Nwns} = \mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\cdot\mathbf{n}_s \quad \text{for } \mathbf{x} \in \Omega_{wns} \tag{4.85}$$

and

$$\kappa_{Gwns} = \mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}\cdot\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \tag{4.86}$$

so that Eq. (4.84) may be written

$$\mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns} = \kappa_{Nwns}\mathbf{n}_s + \kappa_{Gwns}\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \; . \tag{4.87}$$

We will also make use of the definitions of the unit tensors with

$$\mathbf{l}'_{ss} = \mathbf{l}_{wns}\mathbf{l}_{wns} + \mathbf{n}_{ws}\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \tag{4.88}$$

and

$$\mathbf{I} - \mathbf{l}_{wns}\mathbf{l}_{wns} = \mathbf{n}_s\mathbf{n}_s + \mathbf{n}_{ws}\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \; . \tag{4.89}$$

Judicious introduction of the identities involving the unit vectors and unit tensors allows for further regrouping of the integrals in Eq. (4.78) to obtain an equation that contains a set of quantities which must be zero since they multiply independent variations over different domains. This equation is

$$
\begin{aligned}
0 = &-\int\limits_{\Omega_{wn}} \left[p_w - p_n + \rho_{wn}\mathbf{g}_{wn}\cdot\mathbf{n}_w - (\nabla'\cdot\mathbf{n}_w)\gamma_{wn}\right]\mathbf{n}_w\cdot\delta\mathbf{x}_{wn}\,\mathrm{d}\mathfrak{r} \\
&-\int\limits_{\Omega_{ws}} \left[p_w + \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s} + \rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_w - (\nabla'\cdot\mathbf{n}_w)\gamma_{ws}\right]\mathbf{n}_w\cdot\delta\mathbf{x}_{ws}\,\mathrm{d}\mathfrak{r} \\
&-\int\limits_{\Omega_{ns}} \left[p_n + \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s} + \rho_{ns}\mathbf{g}_{ns}\cdot\mathbf{n}_n - (\nabla'\cdot\mathbf{n}_n)\gamma_{ns}\right]\mathbf{n}_n\cdot\delta\mathbf{x}_{ns}\,\mathrm{d}\mathfrak{r} \\
&+\int\limits_{\Omega_{ws}} \left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} \left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} \\
&+\int\limits_{\Omega_{ws}} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{ns}} \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ns}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{wns}} \mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{l}'_{ss}\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} \\
&+\int\limits_{\Omega_{wns}} \left(\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s^*{:}\mathbf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_s\,\mathrm{d}\mathfrak{r} \\
&+\int\limits_{\Omega_{wns}} (\gamma_{wn}\cos\varphi_{ws,wn} + \gamma_{ws} - \gamma_{ns} - \rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_{ws} + \gamma_{wns}\kappa_{Gwns})\,\mathbf{n}_{ws}\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r} \\
&-\int\limits_{\Omega_{wns}} \left(\gamma_{wn}\sin\varphi_{wn,ws} + \rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_s - \gamma_{wns}\kappa_{Nwns} - \frac{2\boldsymbol{\sigma}_s^*{:}\mathbf{C}_s}{3j_s}\right)\mathbf{n}_s\cdot\delta\mathbf{x}_{wns}\,\mathrm{d}\mathfrak{r}\,.
\end{aligned}
\tag{4.90}
$$

We now examine the equilibrium conditions that are implied by this equation.

4.6.4 Additional Equilibrium Conditions

Based upon the first integral in Eq. (4.90), the equilibrium condition on the *wn* interface is

$$
p_w - p_n + \rho_{wn}\mathbf{g}_{wn}\cdot\mathbf{n}_w - (\nabla'\cdot\mathbf{n}_w)\gamma_{wn} = 0 \quad \text{for } \mathbf{x}\in\Omega_{wn}\,. \tag{4.91}
$$

This is the Young-Laplace equation [3, 5, 13, 19] for a fluid-fluid interface, supplemented to account for the possibility that $\rho_{wn}\mathbf{g}_{wn}\cdot\mathbf{n}_w$ could be significant. The capillary pressure, p^c_{wn}, is defined as the product of interfacial tension and interfacial curvature according to

$$
p^c_{wn} = -(\nabla'\cdot\mathbf{n}_w)\gamma_{wn}\,. \tag{4.92}
$$

Therefore, under the two conditions that the interfacial mass density is negligible and the system is at equilibrium, Eq. (4.91) provides the relation

$$p_{wn}^{c} = p_n - p_w \, . \tag{4.93}$$

The following conditions are worth listing explicitly:

- Capillary pressure is a state property of a fluid-fluid interface equal to the interfacial tension multiplied by the curvature.
- Capillary pressure is equal to the interfacial pressure difference of the phases on each side of the interface at equilibrium when the interfacial density term is negligible, but it can be identified according to Eq. (4.92) even when pressure equilibrium has not been achieved.
- Identification of a contact angle where a fluid-fluid interface meets a solid surface is not intrinsic to the definition of capillary pressure.

These observations will be revisited subsequently in describing porous media processes at a larger scale.

From the second and third integrals in Eq. (4.90), we obtain the conditions

$$p_w + \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s} + \rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_w - (\nabla'\cdot\mathbf{n}_w)\gamma_{ws} = 0 \quad \text{for } \mathbf{x} \in \Omega_{ws} \tag{4.94}$$

and

$$p_n + \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s} + \rho_{ns}\mathbf{g}_{ns}\cdot\mathbf{n}_n - (\nabla'\cdot\mathbf{n}_n)\gamma_{ns} = 0 \quad \text{for } \mathbf{x} \in \Omega_{ns} \, . \tag{4.95}$$

These conditions are consistent with Eq. (4.52) obtained at the solid surface for the single-fluid-phase case. They express the balance of the normal forces at the solid surface at equilibrium. Based on the fourth and fifth integrals in Eq. (4.90), we deduce

$$\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3j_s} = 0 \quad \text{for } \mathbf{x} \in \Omega_{ws} \text{ or } \mathbf{x} \in \Omega_{ns} \, . \tag{4.96}$$

Therefore, equilibrium conditions Eqs. (4.94) and (4.95) may, alternatively, be expressed as

$$p_w + \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s + \rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_w - (\nabla'\cdot\mathbf{n}_w)\gamma_{ws} = 0 \quad \text{for } \mathbf{x} \in \Omega_{ws} \tag{4.97}$$

and

$$p_n + \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s + \rho_{ns}\mathbf{g}_{ns}\cdot\mathbf{n}_n - (\nabla'\cdot\mathbf{n}_n)\gamma_{ns} = 0 \quad \text{for } \mathbf{x} \in \Omega_{ns} \, . \tag{4.98}$$

The sixth, seventh, and eighth integrals in Eq. (4.90) dictate the equilibrium conditions

$$\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws} = \mathbf{0}' \quad \text{for } \mathbf{x} \in \Omega_{ws} \, , \tag{4.99}$$

$$\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ns} = \mathbf{0}' \quad \text{for } \mathbf{x} \in \Omega_{ns} \, , \tag{4.100}$$

and

$$\mathbf{n}_s\cdot\mathbf{t}_s^{*}\cdot\mathbf{l}'_{ss} = \mathbf{0}' \quad \text{for } \mathbf{x} \in \Omega_{wns} \, . \tag{4.101}$$

These equations express the conditions on the lateral stress on the solid surface, including at common curve locations, and replicate the findings of Eq. (4.54) for the single-fluid-phase case on the solid surface, though no common curve exists for that case.

The last three integrals in Eq. (4.90) involve the independent variations on the common curve. The multipliers of these variations must be zero, so three equilibrium conditions can be obtained. The first of these is

$$\mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s^* : \mathbf{C}_s}{3 j_s} = 0 \quad \text{for } \mathbf{x} \in \Omega_{wns} \, . \tag{4.102}$$

This equation provides an alternative representation of an equilibrium concentrated force acting at a common curve.

The second condition, which is an extension of the Young equation [1, 17, 19], gives a balance of forces acting on the common curve normal to the curve and tangent to the solid surface. This equation is

$$\gamma_{wn} \cos \varphi_{ws,wn} + \gamma_{ws} - \gamma_{ns} - \rho_{wns} \mathbf{g}_{wns} \cdot \mathbf{n}_{ws} + \gamma_{wns} \kappa_{Gwns} = 0 \quad \text{for } \mathbf{x} \in \Omega_{wns} \, . \tag{4.103}$$

The first three terms comprise those most commonly associated with the Young equation, while the last two are extensions. The terms involving surface tensions account for the lateral forces exerted on the curve by the interfaces. The fourth term is the gravitational force tangent to the solid surface, which would be important only if the common curve mass density is significant. The fifth term accounts for a tendency of the common curve to locate on the surface due to common curve tension and the geodesic curvature. This force is similar to the tendency of a string circle being shortened around a sphere to slide along the surface to a smaller region rather than stay put and become tightened (except at the equator of the sphere).

The final equilibrium condition is a balance of forces at the common curve in the direction normal to the solid surface and is obtained from the last integral in Eq. (4.90) as

$$-\gamma_{wn} \sin \varphi_{wn,ws} - \rho_{wns} \mathbf{g}_{wns} \cdot \mathbf{n}_s + \gamma_{wns} \kappa_{Nwns} + \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s = 0 \quad \text{for } \mathbf{x} \in \Omega_{wns} \, , \tag{4.104}$$

where equilibrium Eq. (4.102) has been invoked to replace $2\boldsymbol{\sigma}_s^* : \mathbf{C}_s / 3 j_s$. The first term in this equation is the normal force exerted by the *wn* interface on the solid surface at the common curve. The second term accounts for the gravitational force exerted in the direction normal to the surface on a common curve with non-zero mass density. The third term is a normal force exerted due to the tension of the common curve. The final term is the normal stress at the solid surface due to the interaction of the common curve with the solid.

The conditions discussed in this subsection, along with the conditions in subsection 4.6.2, provide the set of microscale equilibrium conditions for a porous medium system comprised of two fluids and an elastic solid. These conditions are important for microscale modeling of processes within the solid and the pore space. When modeling at the macroscale, appropriately scaled averages of these conditions must also be satisfied.

4.7 Summary

In this chapter, we have examined the conditions that hold at equilibrium in microscale porous medium systems using a variational analysis. The generality of this method makes it attractive for analysis of multiphase systems, although it is not commonly employed in the porous medium literature. The mathematical elements that provide insights into and background for the variational analysis applied here is provided in Appendix A. The variational problem was formulated as one for which the equilibrium state has minimum internal energy, maximum entropy, and no chemical reactions occurring. Based on a CIT formulation of the material thermodynamics, equilibrium analyses were performed for single-fluid-phase and for two-fluid-phase porous medium systems with an elastic solid.

The equilibrium conditions derived in this chapter will guide the formulation of closed models at both the microscale and, with some additional work, at the macroscale. The methods employed are general, powerful, and applicable to other systems that may be of interest.

Exercises

4.1. Derive the following variational relations that are given in Table 4.1. (Note: Some of these derivations are more challenging than others!)

a. Jacobian:

$$\delta j_\alpha = j_\alpha \nabla\cdot\delta\mathbf{x}_\alpha \,.$$

b. Unit normal vector to surface of phase α with $\delta\mathbf{x}_{\alpha\alpha}$ being the variation of the location of the surface of the phase:

$$\delta\mathbf{n}_\alpha = -\left(\nabla'\delta\mathbf{x}_{\alpha\alpha}\right)\cdot\mathbf{n}_\alpha \,.$$

c. Surface curvature:

$$\overline{\delta}' J_{\alpha\beta} = -\left(\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\beta}\right)\left(J^2_{\alpha\beta} - 2K_{\alpha\beta}\right) - \nabla'\cdot\left[\nabla'\left(\mathbf{n}_\alpha\cdot\delta\mathbf{x}_{\alpha\beta}\right)\right] \,,$$

where the second curvature, $K_{\alpha\beta}$ is defined as

$$2K_{\alpha\beta} = J^2_{\alpha\beta} - (\nabla'\mathbf{n}_\alpha){:}(\nabla'\mathbf{n}_\alpha) \,. \tag{4.105}$$

d. Surface gravitational potential:

$$\overline{\delta}' \psi_{\alpha\beta} = -\mathbf{g}_{\alpha\beta} \cdot \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \delta \mathbf{x}_{\alpha\beta} \; .$$

4.2. Obtain the equilibrium conditions for a single-phase system composed only of a fluid.

4.3. Obtain the equilibrium conditions for a single-phase system composed only of an elastic solid.

4.4. Show that for an elastic solid phase, the equilibrium condition given by Eq. (4.51) as

$$\nabla \cdot \mathbf{t}_s - \rho_s \nabla \left(\frac{\mathbf{t}_s : \mathbf{I}}{3\rho_s} \right) = \mathbf{0}$$

is consistent with the equilibrium condition required by the microscale momentum balance obtained from Eq. (2.27) as

$$\nabla \cdot \mathbf{t}_s + \rho_s \mathbf{g}_s = \mathbf{0} \; .$$

4.5. Show that making use of the equilibrium condition given by Eq. (4.50) and the Gibbs-Duhem equation given by Eq. (3.143), one can re-express equilibrium condition Eq. (4.51) as

$$\left\langle \nabla \cdot \mathbf{t}_s - \nabla \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \right\rangle_{\Omega_s, \Omega_s} = \mathbf{0} \; . \tag{4.106}$$

4.6. Prove the identity given as Eq. (4.84),

$$\nabla'' \cdot \mathbf{l}''_{wns} = \mathbf{l}_{wns} \cdot \nabla'' \mathbf{l}_{wns} = \mathbf{l}_{wns} \cdot \nabla'' \mathbf{l}_{wns} \cdot \mathbf{n}_s \mathbf{n}_s + \mathbf{l}_{wns} \cdot \nabla'' \mathbf{l}_{wns} \cdot \mathbf{n}_{ws} \mathbf{n}_{ws} \; .$$

4.7. Obtain the conditions of equilibrium for a three-fluid-phase system with no solid phase. (Hint: for a three-fluid-system, the boundary surfaces of the phases will not necessarily be smooth at the common curve, and the fluid phases do not sustain a concentrated force at the curve.)

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Chapter 5
Microscale Closure for a Fluid Phase

5.1 Overview

The TCAT approach outlined in Fig. 1.3 includes many interrelated components, including conservation and balance equations, thermodynamics, equilibrium conditions, entropy inequalities, and closure relations. Each of these components must be established at the scale of interest. If the scale of interest is the microscale, then all the necessary components to build a complete, closed, mechanistic model are available from the preceding chapters. In the present chapter, we will illustrate how these components can be employed to deduce a range of models. The concepts will be employed to analyze relatively simple cases that, nevertheless, have wide applicability to continuum modeling of real systems.

Because the models considered in this chapter are at the microscale, a simplified version of the general multiscale model formulation procedure outlined in Fig. 1.3 is possible. The simplification that occurs is depicted in Fig. 5.1 where the elements needed for a macroscale formulation have been deleted. The simplifications occur because there is no need to change the scale of conservation and balance laws formulated at the microscale and because no geometric evolution equations, as approximated from averaging theorems, arise. This latter simplification occurs because the locations of phases and the interfaces between phases are determined in detail in a microscale model. In contrast, at the macroscale the distribution of phases and interfaces is only accounted for in an average sense. At either scale, the determination of the distribution of entities in a multiphase porous medium system is one of the most challenging aspects of the problem in comparison to the case of flow of fluids where all interfaces are fixed.

Mechanistic models are formulated as systems of conservation equations and closure relations, with the former being exact, subject to a mild set of restrictions, and the latter being approximate, non-unique mathematical constructs. The thermodynamically constrained approach developed here assures consistency of the approximations with the second law of thermodynamics by generating a set of necessary conditions that must be satisfied by posited closure relations. The forms of these

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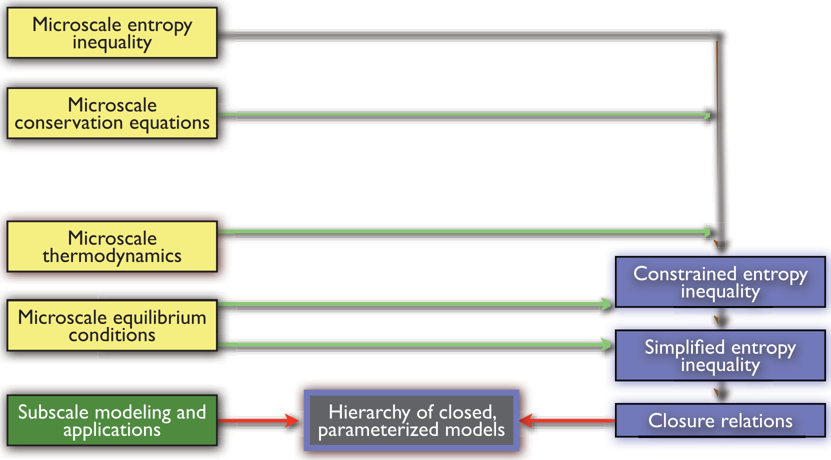

Fig. 5.1 Conceptual representation of the microscale closure approach (after [2])

closure relations may be suggested and supported by experimental observations, theoretical considerations (e.g., statistical mechanics, kinetic theory), or subscale simulations (e.g., molecular dynamics). Because approximations are involved in formulating closure relations, a hierarchy of models of varying sophistication can be obtained depending on the the complexity and accuracy of those approximations.

The need for closure relations lies in the fact that there are more unknowns in the conservation equations than there are equations. The closure procedure typically replaces an unknown function with a functional form that depends on system variables and some additional parameters. If the parameters assume essentially constant values over a range of operating conditions for a particular system, the replacement of the unspecified function with the closure relation is useful. A closure relation for which the parameter values must be varied dramatically over a narrow range of operating conditions of a system in order to model system behavior is not useful as this situation suggests that the underlying mechanisms that account for system behavior are not being properly captured. However, some systems have an inherent variation in physical properties that necessarily requires physical parameters to vary, often markedly, even for carefully constructed models. Such heterogeneous systems are not the focus of this work.

Because of the need to test the robustness and range of applicability of a closure relation for a mechanistic model, it is appropriate and beneficial for a model formulation framework to be posed in terms of a formal mathematical structure. Such a structure should provide pathways for model improvements so that refinements can be made iteratively. Iterations involve working to ensure that the sophistication of the model matches the complexity of the active mechanisms of the application being considered. When this is the case, the mechanistic model will yield a useful description of the physical system.

The mathematical structure employed here makes use of general conservation and thermodynamic equations that are focused for particular applications by use of primary restrictions, secondary restrictions, approximations, and closure approximations. The primary restrictions describe the basic components (i.e., number of species, types of entities, etc.) of a class of system of concern. These primary restrictions dictate the set of conservation, balance, and thermodynamic equations that must be employed in formulating a constrained entropy inequality (CEI). The CEI is developed from the conservation and thermodynamic relations without any additional mathematical approximations. Model closure requires formulation of a simplified entropy inequality (SEI), which is based on the CEI but makes use of various mathematical and physical approximations. These approximations are informed by equilibrium conditions, which assist in arranging the entropy inequality to a form involving products of independent fluxes and forces. All forces and fluxes are zero at equilibrium, such that entropy generation, which is accounted for by these products, is also zero at equilibrium. Finally, the SEI is used as a constraint on the forms of closure relations. The closure relations postulated are approximate and not unique but serve as possibly useful expressions. The forms obtained can then be checked for validity through a model validation investigation.

This mathematical structure will be demonstrated by examining a specific example of a single-fluid-phase system in the following sections. The example shows how the approaches summarized in the various boxes in Fig. 5.1 are employed to derive a closed model. The steps employed can be applied to other systems as desired.

5.2 System Definition

As an example of a microscale system to be analyzed, we consider a single fluid phase, denoted as w. The system is not necessarily isothermal. Additionally, phase w may be composed of more than one chemical species, with the index set of chemical species $\mathfrak{I}_s$. The chemical species may react and may be distributed non-uniformly in the system. Because the analysis is at the microscale, a point in the system contains only phase w, and the domain of study is Ω_w. The boundary of this domain, Γ_w, could be composed of interfaces with other phases or could be simply an external boundary when no other phases are present. This system is posed using two primary restrictions.

Primary Restriction 5.1 (System and Scale) *The system of concern consists of a single fluid phase w in domain Ω_w with boundary Γ_w composed of N chemical species with index set $i \in \mathfrak{I}_s$. The spatial scale of concern is the microscale, ℓ_{mi}, with $\ell_{\mathrm{mo}} \ll \ell_{\mathrm{mi}} \ll \ell_{\mathrm{r}}^{\mathrm{r}}$ where ℓ_{mo} and $\ell_{\mathrm{r}}^{\mathrm{r}}$ are the molecular and resolution scales of the system.*[1]

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[1] Recall the descriptions of length scales provided in conjunction with Eq. (1.1).

Primary Restriction 5.2 (Phenomena Modeled) *The phenomena to be modeled consist of the transport of the mass of the chemical species comprising the w phase and of the momentum and energy of the w phase as functions of space and time.*

These primary restrictions specify the system to be considered, stipulate the length scale at which phenomena will be described, and indicate the phenomena to be modeled. These restrictions are important in identifying the conservation equations to be selected to describe the system. These restrictions are helpful in focusing attention on a system of interest such that the appropriate generality of the system description can be obtained. For example, one could seek a model for the momentum of the chemical species in the system rather than for the momentum of the phase as a whole. Although such an analysis is possible and provides a more general set of equations than those stipulated in Primary Restriction 5.2, the additional mathematical effort required for the derivation and subsequent experimental and computational studies of the posited closure relations may not be worthwhile for many cases.

Thermodynamic considerations also require that an appropriate thermodynamic theory be chosen and applicable to the system of concern. We will use CIT for all models considered, including the microscale models of concern in this chapter. This approach can be formulated as a primary restriction.

Primary Restriction 5.3 (Thermodynamic Basis) *Classical irreversible thermodynamics (CIT) provides an accurate description of the equilibrium and near-equilibrium states of the microscale system.*[2]

This primary restriction means that we will make use of a relatively simple thermodynamic description of the system. This precludes modeling some high frequency phenomena, systems with memory, and processes where the local equilibrium assumption does not apply. These limitations are not important to a wide array of phenomena, but a different thermodynamic framework can be employed if need be.

In light of these primary restrictions, we now turn to the task of formulating the closure relations for fluid *w* based on the conservation equations from Chap. 2, thermodynamic formulas from Chap. 3, and the equilibrium relations from Chap. 4. This will be accomplished by focusing sequentially on each of the boxes and arrows in Fig. 5.1.

5.3 Conservation and Thermodynamic Equations

The starting point for development of a closed mechanistic model for the fluid phase *w* will be the identification of the equations that comprise the elements of the three boxes in the top left corner of Fig. 5.1. In an effort to minimize the length of equations while still retaining clarity, we will, when possible, make use of the symbolism employed previously to indicate equations rather than writing the full equations

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[2] The issue of "nearness" to equilibrium has been discussed in Sect. 3.11.

(e.g., $\mathcal{M}_{iw} = 0$ as obtained from Eq. (2.17) or Table 2.1). The conservation equations for a fluid phase are found in Sect. 2.3.2 while the thermodynamic relations rely on Sects. 3.4 and 3.11.

5.3.1 Entropy Inequality

The entropy inequality is the first system element identified in Fig. 5.1. The primary restrictions turn our attention to a fluid system comprised of multiple species. For the single-fluid-phase system, the entropy balance for each chemical species is obtained from the last row of of Table 2.1 as

$$\mathcal{S}_{*iw} = \Lambda_{iw} \quad \text{for } i \in \mathfrak{I}_s \, , \tag{5.1}$$

where Λ_{iw} is the rate of entropy production at a microscale point associated with species i in phase w. The second law of thermodynamics requires that entropy production at a point be non-negative. However, each microscale point is "occupied" by more than one species. Thus, we cannot say whether Λ_{iw} will be non-negative. However if we sum over all species at the point, we will obtain an entropy balance such that

$$\sum_{i \in \mathfrak{I}_s} \mathcal{S}_{*iw} = \mathcal{S}_{*w} = \sum_{i \in \mathfrak{I}_s} \Lambda_{iw} = \Lambda_w \geq 0 \, . \tag{5.2}$$

The fact that the inequality is non-negative asserts that irreversible processes involving all chemical constituents will produce entropy at a location while, at equilibrium, $\Lambda_w = 0$. Note that the expression for $\mathcal{S}_{*w}$ may be obtained equivalently as the sum of expressions for $\mathcal{S}_{*iw}$ in Table 2.1 or directly from the last line of Table 2.2. At this point in the development, we will write the entropy inequality as

$$\sum_{i \in \mathfrak{I}_s} \mathcal{S}_{*iw} = \Lambda_w \geq 0 \, . \tag{5.3}$$

Should we decide to work with only the entity of the w phase as a whole, then this expression may be written in the form

$$\mathcal{S}_{*w} = \Lambda_w \geq 0 \, . \tag{5.4}$$

Our quest here is to obtain an expression for Λ_w in terms of the fluxes and the forces that drive those fluxes in the system of interest, thereby generating entropy. To achieve this objective, it is necessary to consider the implications of the conservation equations on allowable system behavior and to identify the appropriate equations.

5.3.2 Conservation Equations

The second box in the top left corner of Fig. 5.1 is the conservation equations. Conservation equations for mass, momentum, and energy of each chemical species have been obtained and are provided in Table 2.1. For the mass conservation of the species, the equations in material derivative form are denoted as

$$\mathcal{M}_{*iw} = 0 \quad \text{for } i \in \mathfrak{I}_s\ ; \tag{5.5}$$

for momentum conservation we have

$$\mathcal{P}_{*iw} = \mathbf{0} \quad \text{for } i \in \mathfrak{I}_s\ ; \tag{5.6}$$

and the total energy of each species is conserved according to

$$\mathcal{E}_{*iw} = 0 \quad \text{for } i \in \mathfrak{I}_s\ . \tag{5.7}$$

Note that we have N scalar conservation equations for both chemical species and energy along with $3N$ components of the vector momentum equation.

One additional equation from Table 2.1 that we will employ is the expression for the body force potential, taken here to be the gravitational potential. This equation is denoted as

$$\mathcal{G}_{*iw} = 0 \quad \text{for } i \in \mathfrak{I}_s\ . \tag{5.8}$$

Strictly speaking, this is not a conservation equation but is a balance equation that has been obtained by making use of conservation of mass and the relation between the body force potential and the body force per unit mass.

5.3.3 Thermodynamic Relations

The third box in Fig. 5.1 is the thermodynamic identities. Here we have elected to employ the CIT thermodynamic framework. With the assumptions inherent in this formulation as an extension to classical equilibrium thermodynamics, we are able to write relations among the rates of change of thermodynamic variables. For a species in a fluid phase, the appropriate rate of change expression is that given in the first line of Table 3.1. Thus the thermodynamic expression is

$$\mathcal{T}_{*iw} = 0 \quad \text{for } i \in \mathfrak{I}_s\ . \tag{5.9}$$

The body force potential for a species in the w phase, Ψ_{iw}, equals $\rho_w \omega_{iw} \psi_{iw}$, as given by Eq. (2.44) with α replaced by w. Therefore the material derivative of Ψ_{iw} is related to the material derivatives of the independent variables according to Eq. (2.45), which may be written

$$\mathcal{T}_{\mathcal{G}*iw} = 0 \quad \text{for } i \in \mathfrak{I}_s\ . \tag{5.10}$$

Because it is a form that relates only material derivatives, this equation is collected here in the thermodynamic section. Indeed, it relates the material derivative of potential energy to other system variables.

5.4 Constrained Entropy Inequality

According to Fig. 5.1, the next step in the microscale closure approach is to combine the entropy inequality with the conservation and balance equations as well as the thermodynamic equations to obtain a constrained entropy inequality. The conservation, balance, and thermodynamic equations are the relations that supplement the physics described by the entropy equation by ensuring that the entropy generation process does not violate other physical principles. Several steps are involved in constraining the entropy inequality so that it provides the entropy generation in terms of irreversible processes. These steps will be followed here.

5.4.1 Introduction of Constraints

Entropy production is a result of dissipative processes such as heat conduction, the flow of matter, mechanical dissipation, chemical reactions, and electrical currents leading to irreversible processes [5]. Because of these entropy-producing processes, the entropy production rate is typically represented as the product of a set of thermodynamic fluxes and thermodynamic forces such that for a system,

$$\Lambda = \sum_{i\in\mathcal{P}_s} J_i F_i + \sum_{j\in\mathcal{P}_v} \mathbf{J}_j\cdot\mathbf{F}_j + \sum_{k\in\mathcal{P}_t} \mathsf{J}_k:\mathsf{F}_k\,, \tag{5.11}$$

where J_i, $\mathbf{J}_j$, and J_k are thermodynamic fluxes corresponding to scalar, vector, and tensor types, respectively; F_i, $\mathbf{F}_j$, and F_k are thermodynamic forces of the scalar, vector, and tensor types, respectively; and $\mathcal{P}_s$, $\mathcal{P}_v$, and $\mathcal{P}_t$ are index sets of scalar, vector, and tensor dissipative processes that produce entropy.

An important property of Eq. (5.11) is that each factor in all products must be zero at equilibrium—the state of minimum energy, maximum entropy, and zero entropy production rate. Another property is that each member of the set of fluxes must be independent of all other fluxes, and each member of the set of forces must be independent of all other forces. Collectively, this is referred to as the flux-force independence condition. Because of the symmetry required by the flux-force independence condition, the identification of each factor in the products given in Eq. (5.11) as a "force" or "flux" is arbitrary as long as the independence condition is met [5]. However, in some instances it is more convenient to define a particular factor as a force rather than a flux, or vice versa. These considerations lead to formulation of an entropy production postulate:

Postulate 5.1 (Entropy Production Postulate, EPP) *The rate of production of entropy, Λ, may be expressed as a sum of inner products of members of a set of fluxes $\mathfrak{J}$ and conjugate members of a companion set of forces $\mathfrak{F}$ with both $\mathfrak{J}$ and $\mathfrak{F}$ comprised of members that are zero at equilibrium and independent of all other members in the respective set but which can depend upon one or more members of the companion set.*

The EPP provides guidance for the development of a form of the entropy inequality (EI) that will be of most use in developing closure relations, and it leads to linearized approximations for a set of fluxes in terms of members of a set of mutually independent forces in the near-equilibrium regime. It is important that the forces and fluxes that we identify as "independent" indeed be independent. We are guided in this pursuit by insight into the system summarized by the equilibrium conditions developed in Chap. 4. Our goal is thus to develop an EI that is in strict force-flux form. This form will be used to aid the development of closure relations needed to produce well-posed models.

For the single-phase system specifically being considered here, the entropy balance is given by Eq. (5.3). This is an equation that provides the elements of the entropy production rate in terms of entropy transport, but it does not give the entropy production rate in the form of Eq. (5.11). Thus we seek to alter the form of the entropy balance while preserving the inequality that it provides.

If quantities that are equal to zero are added to the left side of Eq. (5.3), the inequality will not be altered. Thus we may add the conservation, balance, and thermodynamic expressions to this equation, each multiplied by an arbitrary Lagrange multiplier, which can be selected to ensure dimensional consistency and to facilitate the arrangement of contributions to Λ_w into force-flux form. Thus, Eq. (5.3) is augmented to produce the expression

$$\sum_{i\in\mathfrak{I}_s} \mathcal{S}_{*iw} + \sum_{i\in\mathfrak{I}_s} \lambda_{\mathcal{E}iw}\mathcal{E}_{*iw} + \sum_{i\in\mathfrak{I}_s} \boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}iw}\cdot\boldsymbol{\mathcal{P}}_{*iw} + \sum_{i\in\mathfrak{I}_s} \lambda_{\mathcal{M}iw}\mathcal{M}_{*iw} \\ + \sum_{i\in\mathfrak{I}_s} \lambda_{\mathcal{G}iw}\mathcal{G}_{*iw} + \sum_{i\in\mathfrak{I}_s} \lambda_{\mathcal{T}iw}\mathcal{T}_{*iw} + \sum_{i\in\mathfrak{I}_s} \lambda_{\mathcal{T}\mathcal{G}iw}\mathcal{T}_{\mathcal{G}*iw} = \Lambda_w \geq 0\,, \quad (5.12)$$

where the subscripted λ's and $\boldsymbol{\lambda}$ are Lagrange multipliers, and the equation forms are as indicated in the preceding section.

It is possible at this point to formulate a strategy for determining the Lagrange multipliers en route to a closed, detailed description of the system that includes the full dynamics of each species in the system. However, proceeding on this route carries a large overhead in the number of coefficients and functional forms that will have to be determined in closing the system. For example, we would have to determine and parameterize stress tensors, heat conduction vectors, and other fluxes for each of the chemical species. Rather than following this complicated path, we will restrict the analysis to a simpler approach, noting that if the resulting relations are inadequate for describing the system, we can revert back to a more complete analysis. Primary Restriction 5.2 states that the model to be employed will make use of species mass balance equations but will assume that the momentum and energy transport in the system can be accounted for on an entity basis. This restriction is enforced by selecting the Lagrange multipliers as

$$\lambda_{\mathcal{E}iw} = \lambda_{\mathcal{E}w} \quad \text{for } i \in \mathfrak{I}_s \,, \tag{5.13}$$

$$\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}iw} = \boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}w} \quad \text{for } i \in \mathfrak{I}_s \,, \tag{5.14}$$

$$\lambda_{\mathcal{G}iw} = \lambda_{\mathcal{G}w} \quad \text{for } i \in \mathfrak{I}_s \,, \tag{5.15}$$

$$\lambda_{\mathcal{T}iw} = \lambda_{\mathcal{T}w} \quad \text{for } i \in \mathfrak{I}_s \,, \tag{5.16}$$

and (5.17)

$$\lambda_{\mathcal{T}\mathcal{G}iw} = \lambda_{\mathcal{T}\mathcal{G}w} \quad \text{for } i \in \mathfrak{I}_s \,. \tag{5.18}$$

To see how these choices affect the constrained entropy inequality, we substitute the Lagrange multipliers that are independent of species into Eq. (5.12) and move the multipliers that no longer depend on i outside the summations to obtain

$$\sum_{i\in\mathfrak{I}_s} \mathcal{S}_{*iw} + \lambda_{\mathcal{E}w} \sum_{i\in\mathfrak{I}_s} \mathcal{E}_{*iw} + \boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}w} \cdot \sum_{i\in\mathfrak{I}_s} \boldsymbol{\mathcal{P}}_{*iw} + \sum_{i\in\mathfrak{I}_s} \lambda_{\mathcal{M}iw} \mathcal{M}_{*iw}$$
$$+ \lambda_{\mathcal{G}w} \sum_{i\in\mathfrak{I}_s} \mathcal{G}_{*iw} + \lambda_{\mathcal{T}w} \sum_{i\in\mathfrak{I}_s} \mathcal{T}_{*iw} + \lambda_{\mathcal{T}\mathcal{G}w} \sum_{i\in\mathfrak{I}_s} \mathcal{T}_{\mathcal{G}*iw} = \Lambda_w \geq 0 \,. \tag{5.19}$$

The summations over species-based equations have been shown to result in the entity-based equations. Thus, performing the summations as possible we obtain

$$\mathcal{S}_{*w} + \lambda_{\mathcal{E}w} \mathcal{E}_{*w} + \boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}w} \cdot \boldsymbol{\mathcal{P}}_{*w} + \sum_{i\in\mathfrak{I}_s} \lambda_{\mathcal{M}iw} \mathcal{M}_{*iw}$$
$$+ \lambda_{\mathcal{G}w} \mathcal{G}_{*w} + \lambda_{\mathcal{T}w} \mathcal{T}_{*w} + \lambda_{\mathcal{T}\mathcal{G}w} \mathcal{T}_{\mathcal{G}*w} = \Lambda_w \geq 0 \,. \tag{5.20}$$

The conservation and balance equations that are denoted in this equation, on an entity basis for all properties except mass, have already been developed and their expanded forms can be substituted in.

5.4.2 *Selection of Lagrange Multipliers*

Because the Lagrange multipliers each multiply an expression that is equal to zero, the values of the multipliers can be selected arbitrarily without impacting the correctness of Eq. (5.20). However, it is our objective here to arrive at an expression for Λ_w that consists of products of independent fluxes and forces that drive those fluxes. This is achieved by eliminating material derivatives from the expression as far as possible. Equations for $\mathcal{S}_{*w}$, $\mathcal{E}_{*w}$, $\boldsymbol{\mathcal{P}}_{*w}$, and $\mathcal{G}_{*w}$ are taken from Table 2.2; the equation for $\mathcal{M}_{*iw}$ is given in Table 2.1; the equation for $\mathcal{T}_{\mathcal{G}*w}$ is Eq. (2.48) with $\alpha = w$; and the expression for $\mathcal{T}_{*w}$ is the fifth row of entries in Table 3.1.

We substitute the appropriate expressions into Eq. (5.20). However, for the moment we are interested in eliminating the material time derivatives. Therefore, only these terms are listed in the following equation with the remaining terms designated simply using ellipses. With this convention, Eq. (5.20) becomes

$$\begin{aligned}
&\left[\frac{\mathrm{D}_w\eta_w}{\mathrm{D}t}+\ldots\right]+\lambda_{\mathcal{E}w}\left\{\frac{\mathrm{D}_w}{\mathrm{D}t}\left[E_w+\rho_w\left(\frac{\mathbf{v}_w\cdot\mathbf{v}_w}{2}+K_{Ew}\right)\right]+\ldots\right\}\\
&+\boldsymbol{\lambda}_{\mathcal{P}w}\cdot\left[\frac{\mathrm{D}_w(\rho_w\mathbf{v}_w)}{\mathrm{D}t}+\ldots\right]+\sum_{i\in\mathfrak{J}_s}\lambda_{\mathcal{M}iw}\left[\frac{\mathrm{D}_{iw}(\rho_w\omega_{iw})}{\mathrm{D}t}+\ldots\right]\\
&+\lambda_{\mathcal{G}w}\left[\frac{\mathrm{D}_w\Psi_w}{\mathrm{D}t}+\ldots\right]+\lambda_{\mathcal{T}w}\left[\frac{\mathrm{D}_wE_w}{\mathrm{D}t}-\theta_w\frac{\mathrm{D}_w\eta_w}{\mathrm{D}t}-\sum_{i\in\mathfrak{J}_s}\mu_{iw}\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}\right]\\
&+\lambda_{\mathcal{T}\mathcal{G}w}\left[\frac{\mathrm{D}_w\Psi_w}{\mathrm{D}t}-\sum_{i\in\mathfrak{J}_s}\psi_{iw}\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}-\sum_{i\in\mathfrak{J}_s}\rho_w\omega_{iw}\frac{\mathrm{D}_w\psi_{iw}}{\mathrm{D}t}\right]=\Lambda_w\geq 0\,.
\end{aligned}\tag{5.21}$$

Some of the time derivatives in Eq. (5.21) can be expressed in terms of other variables or expanded using the product rule. These changes are pursued so that the number of independent time derivatives is minimized. The relations employed are

$$\frac{\mathrm{D}_w}{\mathrm{D}t}\left(\rho_w\frac{\mathbf{v}_w\cdot\mathbf{v}_w}{2}\right)=\mathbf{v}_w\cdot\frac{\mathrm{D}_w(\rho_w\mathbf{v}_w)}{\mathrm{D}t}-\frac{\mathbf{v}_w\cdot\mathbf{v}_w}{2}\sum_{i\in\mathfrak{J}_s}\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}\,,\tag{5.22}$$

$$\frac{\mathrm{D}_w(\rho_wK_{Ew})}{\mathrm{D}t}=\sum_{i\in\mathfrak{J}_s}\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}+\sum_{i\in\mathfrak{J}_s}\rho_w\omega_{iw}\frac{\mathrm{D}_w}{\mathrm{D}t}\left(\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\,,\tag{5.23}$$

and

$$\frac{\mathrm{D}_{iw}(\rho_w\omega_{iw})}{\mathrm{D}t}=\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}+\mathbf{u}_{iw}\cdot\nabla(\rho_w\omega_{iw})\ .\tag{5.24}$$

In these equations, use has been made of the definitions of variables given in Eqs. (2.24) and (2.35) and of the fact that the sum of the mass fractions in the phase is 1. Substitution of these last three identities into the energy and species conservation parts of Eq. (5.21) yields

$$\begin{aligned}
&\left[\frac{\mathrm{D}_w\eta_w}{\mathrm{D}t}+\ldots\right]+\lambda_{\mathcal{E}w}\left\{\frac{\mathrm{D}_wE_w}{\mathrm{D}t}+\mathbf{v}_w\cdot\frac{\mathrm{D}_w(\rho_w\mathbf{v}_w)}{\mathrm{D}t}-\frac{\mathbf{v}_w\cdot\mathbf{v}_w}{2}\sum_{i\in\mathfrak{J}_s}\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}\right.\\
&\left.+\sum_{i\in\mathfrak{J}_s}\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}+\sum_{i\in\mathfrak{J}_s}\rho_w\omega_{iw}\frac{\mathrm{D}_w}{\mathrm{D}t}\left(\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)+\ldots\right\}\\
&+\boldsymbol{\lambda}_{\mathcal{P}w}\cdot\left[\frac{\mathrm{D}_w(\rho_w\mathbf{v}_w)}{\mathrm{D}t}+\ldots\right]+\sum_{i\in\mathfrak{J}_s}\lambda_{\mathcal{M}iw}\left[\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}+\mathbf{u}_{iw}\cdot\nabla(\rho_w\omega_{iw})+\ldots\right]\\
&+\lambda_{\mathcal{G}w}\left[\frac{\mathrm{D}_w\Psi_w}{\mathrm{D}t}+\ldots\right]+\lambda_{\mathcal{T}w}\left[\frac{\mathrm{D}_wE_w}{\mathrm{D}t}-\theta_w\frac{\mathrm{D}_w\eta_w}{\mathrm{D}t}-\sum_{i\in\mathfrak{J}_s}\mu_{iw}\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}\right]
\end{aligned}$$

$$+\lambda_{\mathcal{TG}w}\left[\frac{\mathrm{D}_w\mathit{\Psi}_w}{\mathrm{D}t} - \sum_{i\in\mathcal{J}_s}\psi_{iw}\frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t} - \sum_{i\in\mathcal{J}_s}\rho_w\omega_{iw}\frac{\mathrm{D}_w\psi_{iw}}{\mathrm{D}t}\right] = \Lambda_w \geq 0\,. \tag{5.25}$$

This equation contains $3N+6$ material derivatives where N is the number of chemical species. These derivatives are the set

$$\mathcal{D} = \left\{\frac{\mathrm{D}_w\eta_w}{\mathrm{D}t}, \frac{\mathrm{D}_wE_w}{\mathrm{D}t}, \frac{\mathrm{D}_w(\rho_w\mathbf{v}_w)}{\mathrm{D}t}, \frac{\mathrm{D}_w\mathit{\Psi}_w}{\mathrm{D}t}, \frac{\mathrm{D}_w(\rho_w\omega_{iw})}{\mathrm{D}t}, \frac{\mathrm{D}_w}{\mathrm{D}t}\left(\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right), \frac{\mathrm{D}_w\psi_{iw}}{\mathrm{D}t}\right\} \quad \text{for } i\in\mathcal{J}_s\,, \tag{5.26}$$

where the third element in this set is a three component vector, and the fifth through seventh elements each contain N components. However, the sixth element consists of only $N-1$ independent material derivatives (because of Eq. (2.25)). On the other hand, Eq. (5.25) contains $7+N$ Lagrange multipliers in the set

$$\mathcal{L} = \{\lambda_{\mathcal{E}w}, \boldsymbol{\lambda}_{\mathcal{P}w}, \lambda_{\mathcal{M}iw}, \lambda_{\mathcal{G}w}, \lambda_{\mathcal{T}w}, \lambda_{\mathcal{TG}w}\} \quad \text{for } i\in\mathcal{J}_s\,, \tag{5.27}$$

where the vector $\boldsymbol{\lambda}_{\mathcal{P}w}$ has three components, and there are N components of $\lambda_{\mathcal{M}iw}$. Because the material derivatives of $\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}$ and $\psi_{i\alpha}$ each appear only once in Eq. (5.25), it will not be possible to eliminate them from the equation unless the Lagrange multipliers of their time derivatives are set to zero. Thus we will ignore the last two elements of the set in Eq. (5.26), leaving $6+N$ material derivatives, one less than the number of Lagrange multipliers. This extra multiplier must be chosen judiciously.

Recall that in Chap. 4, equilibrium conditions were determined by examining the variation of the internal plus potential energies. If we set

$$\lambda_{\mathcal{TG}w} = \lambda_{\mathcal{T}w}\,, \tag{5.28}$$

the last two terms in brackets in Eq. (5.25) will combine to give an expression for the derivative of $E_w + \mathit{\Psi}_w$ in terms of the variables on which this sum depends. Thus, we make this selection.

We can now write a linear algebra form to determine the Lagrange multipliers that will eliminate the $6+N$ material derivatives,

$$\left[\begin{array}{c|c|c|c|c} 1 & 0 & 0 & \left(\dfrac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2} - \dfrac{\mathbf{v}_w\cdot\mathbf{v}_w}{2}\right) & -\mu_{iw} - \psi_{iw} \\ 0 & 1 & \mathbf{v}_w & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & -\theta_w \end{array}\right] \left\{\begin{array}{c} \lambda_{\mathcal{M}iw} \\ \boldsymbol{\lambda}_{\mathcal{P}w} \\ \lambda_{\mathcal{E}w} \\ \lambda_{\mathcal{G}w} \\ \lambda_{\mathcal{T}w} \end{array}\right\} = \left\{\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ -1 \end{array}\right\}. \tag{5.29}$$

The rows of the matrix are formed, in order, by collecting coefficients of the material derivatives of the densities of species mass, momentum, internal energy, body force potential, and entropy. We have compressed the N species mass densities and the three momentum terms to a single line, noting that these equations are of a similar form.

Since Eq. (5.29) is in upper triangular form, it may be readily solved by inspection for the Lagrange multipliers to obtain

$$\left\{\begin{array}{c}\lambda_{\mathcal{M}iw}\\ \boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}w}\\ \lambda_{\mathcal{E}w}\\ \lambda_{\mathcal{G}w}\\ \lambda_{\mathcal{T}w}\end{array}\right\}=\frac{1}{\theta_w}\left\{\begin{array}{c}\mu_{iw}+\psi_{iw}-\dfrac{\mathbf{v}_w\cdot\mathbf{v}_w}{2}+\dfrac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\\ \mathbf{v}_w\\ -1\\ -1\\ 1\end{array}\right\}. \tag{5.30}$$

These results are then substituted back into Eq. (5.20) to obtain the augmented entropy inequality

$$\begin{aligned}\mathcal{S}_{*w}-\frac{1}{\theta_w}\mathcal{E}_{*w}+\frac{\mathbf{v}_w}{\theta_w}\cdot\boldsymbol{\mathcal{P}}_{*w}+\frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_s}\left(\mu_{iw}+\psi_{iw}-\frac{\mathbf{v}_w\cdot\mathbf{v}_w}{2}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\mathcal{M}_{*iw}&\\ -\frac{1}{\theta_w}\mathcal{G}_{*w}+\frac{1}{\theta_w}\mathcal{T}_{*w}+\frac{1}{\theta_w}\mathcal{T}_{\mathcal{G}*w}=\Lambda_w\geq 0\,.&\end{aligned} \tag{5.31}$$

This general augmented entropy inequality will next be simplified.

5.4.3 Reduction to the CEI

When the indicated conservation and balance equations are substituted into Eq. (5.31), the result is a rather long equation. Fortunately, a number of terms will cancel. For example, the multipliers of the conservation laws have explicitly been selected so that the material derivatives will cancel out. In addition, some other terms will cancel so that the long equation simplifies significantly. There are no particularly subtle algebraic manipulations that have to be performed, with the most complex maneuver being the application of the product rule to a derivative. Thus, we will not provide the step-by-step algebraic details but will only note that if the indicated particular balance and conservation equations are substituted into Eq. (5.31) and terms are cancelled without making any additional approximations, the following result can be obtained with appropriate collection of terms:

$$\begin{aligned}-b_w+\frac{1}{\theta_w}\left[h_w-\sum_{i\in\mathfrak{I}_s}\rho_w\omega_{iw}\frac{\mathrm{D}_w}{\mathrm{D}t}\left(\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\right]&\\ -\nabla\cdot\left\{\boldsymbol{\varphi}_w-\frac{1}{\theta_w}\left[\mathbf{q}_w+\sum_{i\in\mathfrak{I}_s}\left(\mu_{iw}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\rho_w\omega_{iw}\mathbf{u}_{iw}\right]\right\}&\\ +\frac{1}{\theta_w}\left[\left(\eta_w\theta_w-E_w+\sum_{i\in\mathfrak{I}_s}\rho_w\omega_{iw}\mu_{iw}\right)\mathsf{I}+\mathbf{t}_w\right]:\mathbf{d}_w&\end{aligned}$$

$$
\begin{aligned}
&-\frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_s}\rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left(\mu_{iw}+\psi_{iw}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\\
&-\left[\mathbf{q}_w+\sum_{i\in\mathfrak{I}_s}\left(\mu_{iw}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\rho_w\omega_{iw}\mathbf{u}_{iw}\right]\cdot\nabla\left(\frac{1}{\theta_w}\right)\\
&-\frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_s}\left(\mu_{iw}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)r_{iw}=\Lambda_w\geq 0\,. \qquad (5.32)
\end{aligned}
$$

This arrangement of terms is most certainly not unique. It has been motivated by a desire to arrange the equation into a collection of fluxes and forces that are all zero at equilibrium.

Although we could proceed directly with this equation, we will make several substitutions that will provide an alternative expression. First, we make use of the Euler equation for fluid phase energy given in Eq. (3.156), which may be rearranged to

$$
p_w=\eta_w\theta_w-E_w+\sum_{i\in\mathfrak{I}_s}\rho_w\omega_{iw}\mu_{iw}\,, \qquad (5.33)
$$

to simplify the multiplier of $\mathbf{d}_w$ in Eq. (5.32). Second, we make use of Eq. (3.204), subject to the local equilibrium assumption, to obtain

$$
\nabla\mu_{iw}=\nabla\mu_{iw}|_{\theta_w}+\theta_w\left(\overline{H}_{iw}-\mu_{iw}\right)\nabla\left(\frac{1}{\theta_w}\right)\,. \qquad (5.34)
$$

Substitution of these last two equations into Eq. (5.32) yields

$$
\begin{aligned}
&-b_w+\frac{1}{\theta_w}\left[h_w-\sum_{i\in\mathfrak{I}_s}\rho_w\omega_{iw}\frac{\mathrm{D}_w}{\mathrm{D}t}\left(\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\right]\\
&-\nabla\cdot\left\{\boldsymbol{\varphi}_w-\frac{1}{\theta_w}\left[\mathbf{q}_w+\sum_{i\in\mathfrak{I}_s}\left(\mu_{iw}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\rho_w\omega_{iw}\mathbf{u}_{iw}\right]\right\}\\
&+\frac{1}{\theta_w}\left(p_w\mathbf{I}+\mathbf{t}_w\right):\mathbf{d}_w\\
&-\frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_s}\rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left(\mu_{iw}|_{\theta_w}+\psi_{iw}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\\
&-\left[\mathbf{q}_w+\sum_{i\in\mathfrak{I}_s}\left(\overline{H}_{iw}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\rho_w\omega_{iw}\mathbf{u}_{iw}\right]\cdot\nabla\left(\frac{1}{\theta_w}\right)\\
&-\frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_s}\left(\mu_{iw}+\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)r_{iw}=\Lambda_w\geq 0\,. \qquad (5.35)
\end{aligned}
$$

An additional refinement follows from the notion that no mass is created or destroyed by chemical reactions. Chemical reactions involve the conversion of mass contained in a set of reactant species to the equivalent mass contained in a set of product species. In the current system, we are interested in reactions that occur within phase w, commonly referred to as homogeneous phase reactions to distinguish them from heterogeneous reactions that occur at the boundary of the phase. This designation does not require that the phase be homogeneous in composition or temperature but only indicates that the reaction could occur anywhere within the phase. Homogeneous phase reaction equations are provided routinely in chemistry, chemical kinetics, and chemical engineering contexts [e.g., 4, 14, 15] to explain phenomena that have been observed or that can be predicted. Homogeneous reaction equations can be further categorized as describing elementary reactions or complex reactions. Simply put, elementary reactions occur as written while complex reactions involve a number of intermediate steps that can produce species not present when the reaction is completed. Complex reactions are typically described phenomenologically rather than by explicitly listing the details of the reaction mechanism.

The type of reaction does bear on the appropriate form of a chemical reaction rate expression. For example, monomolecular elementary reactions are first order, meaning they depend linearly on the concentration of a single reactant. Elementary reactions resulting from the collision of two different molecules depend linearly on the concentration of each species and are thus second order overall. Elementary reactions resulting from the simultaneous collision of three species are third order reactions. Elementary reactions of higher than third order have not been observed [15], which implies the reasonable notion that the simultaneous collision of four or more molecules is unlikely to occur. Complex reactions can be of integer or a fractional order; so they can take on more elaborate effective reaction rate expressions than elementary reactions.

The individual reactions that contribute to overall production of species i in phase w can be accounted for according to

$$r_{iw} = \sum_{k \in \mathfrak{I}_{\text{rxn}}} \nu_{ik} \text{MW}_i R_{kw} \,, \tag{5.36}$$

where $\mathfrak{I}_{\text{rxn}}$ is the set of N_{rxn} reactions, ν_{ik} is the stoichiometric coefficient for component i in reaction k, MW_i is the molecular weight of species i and R_{kw} is the molar rate of reaction k. Note that ν_{ik} is negative if species i is being consumed in reaction k, positive if species i is being produced in reaction k, and zero if species i does not participate in reaction k. The affinity of reaction k, denoted A_{kw}, is a measure of disequilibrium of the reaction with

$$A_{kw} = \sum_{i \in \mathfrak{I}_s} \mu_{iw} \nu_{ik} \text{MW}_i \,. \tag{5.37}$$

The affinity can be shown to be related to the partial derivative of the Gibbs free energy with respect to the extent of completion of the reaction holding pressure and temperature constant; it is zero at equilibrium [1]. Here, for convenience, we make use of a slight variant of the standard definition of the affinity, denoted A^*_{kw}, where

$$A^*_{kw} = \sum_{i\in\mathfrak{I}_s} \left(\mu_{iw} + \frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right) \nu_{ik}\mathrm{MW}_i \, . \tag{5.38}$$

With these definitions, Eq. (5.36) followed by Eq. (5.38) may be substituted into the last summation in Eq. (5.35) to yield the CEI

$$\begin{aligned}
&-b_w + \frac{1}{\theta_w}\left[h_w - \sum_{i\in\mathfrak{I}_s} \rho_w\omega_{iw}\frac{\mathrm{D}_w}{\mathrm{D}t}\left(\frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\right] \\
&\quad -\nabla\cdot\left\{\boldsymbol{\varphi}_w - \frac{1}{\theta_w}\left[\mathbf{q}_w + \sum_{i\in\mathfrak{I}_s}\left(\mu_{iw} + \frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\rho_w\omega_{iw}\mathbf{u}_{iw}\right]\right\} \\
&\quad +\frac{1}{\theta_w}(p_w\mathbf{I}+\mathbf{t}_w):\mathbf{d}_w - \frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_s}\rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left(\mu_{iw}|_{\theta_w} + \psi_{iw} + \frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right) \\
&\quad -\left[\mathbf{q}_w + \sum_{i\in\mathfrak{I}_s}\left(\overline{H}_{iw} + \frac{\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}}{2}\right)\rho_w\omega_{iw}\mathbf{u}_{iw}\right]\cdot\nabla\left(\frac{1}{\theta_w}\right) \\
&\quad -\frac{1}{\theta_w}\sum_{k\in\mathfrak{I}_{\mathrm{rxn}}} R_{kw}A^*_{kw} = \Lambda_w \geq 0 \, .
\end{aligned} \tag{5.39}$$

We note that the changes made following Eq. (5.32) to arrive at Eq. (5.39) do not alter the essence of the entropy inequality. The rearrangements do have implications on the forms of the closure relations and associated coefficients that will have to be considered. Because closure is an approximate process, the fact that some representations of the approximations will be superior to others should not be surprising. However, for the moment we are getting ahead of the story. Equation (5.39) has been developed based on the entropy inequality, conservation and balance equations, thermodynamic relations in the CIT framework, and selection of the Lagrange multipliers with an eye toward eliminating the material derivatives. The selection of the Lagrange multipliers had the effect of stipulating that the formulation is in terms of species mass balance equations with entity-based momentum and energy equations. No mathematical approximations have been employed such that Eq. (5.39) can serve as a starting point for a range of closure formulations and for study of systems restricted to be less general than that described to this point (e.g., isothermal, single species).

5.5 Simplified Entropy Inequality

The next step in the derivation of closed equations, based on Fig. 5.1, is to make further use of the equilibrium conditions to inform the CEI of Eq. (5.39) so that it provides a form of entropy production consistent with Eq. (5.11).

5.5.1 Introduction of Approximations

The constraint on Lagrange multipliers imposed by Primary Restriction 5.2 led to entity-based forms of the momentum and energy equations rather than their species-based forms in Eq. (5.20). This means that the problem is formulated in terms of a phase velocity, $\mathbf{v}_w$, and $N-1$ independent dispersion velocities, $\mathbf{u}_{iw}$. If Primary Restriction 5.2 had not been imposed, the formulation would have been in terms of the momentum of each of the N species with their velocities, $\mathbf{v}_{iw}$, appearing explicitly in the full set of species-based momentum equations. In fact using entity-based equations is slightly less general, but it reduces the complexity of the closure issue in that, for example, a single closure approximation must be obtained for $\mathbf{t}_w$ rather than closure relations for each of the N tensors, $\mathbf{t}_{iw}$. This simpler approach does carry a penalty in that the non-linear quantities $\mathbf{u}_{iw}\cdot\mathbf{u}_{iw}/2$ for each species arise in CEI Eq. (5.39). The presence of this term is nettlesome and has received some attention [1]. The most common solution to the presence of this term is to assume that the magnitude of the diffusion velocity squared is small relative to the terms with which it is combined such that it can be neglected. This leads to the statement:

SEI Approximation 5.1 (Diffusive kinetic energy) *When entity-based momentum and energy equations are employed in developing the CEI for a multispecies microscale entity α, the quantity $\mathbf{u}_{i\alpha}\cdot\mathbf{u}_{i\alpha}/2$, where $i \in \mathfrak{I}_s$, is considered to have negligible impact on the entropy inequality and may be eliminated.*

Application of this approximation to Eq. (5.39) then gives

$$\begin{aligned}
&-b_w + \frac{1}{\theta_w}h_w - \nabla\cdot\left[\boldsymbol{\varphi}_w - \frac{1}{\theta_w}\left(\mathbf{q}_w + \sum_{i\in\mathfrak{I}_s}\mu_{iw}\rho_w\omega_{iw}\mathbf{u}_{iw}\right)\right] \\
&\quad + \frac{1}{\theta_w}\left(p_w\mathbf{I} + \mathbf{t}_w\right):\mathbf{d}_w - \frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_s}\rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left(\mu_{iw}|_{\theta_w} + \psi_{iw}\right) \\
&\quad - \left(\mathbf{q}_w + \sum_{i\in\mathfrak{I}_s}\overline{H}_{iw}\rho_w\omega_{iw}\mathbf{u}_{iw}\right)\cdot\nabla\left(\frac{1}{\theta_w}\right) - \frac{1}{\theta_w}\sum_{k\in\mathfrak{I}_{\text{rxn}}}R_{kw}A_{kw} = \Lambda_w \geq 0\,.
\end{aligned} \tag{5.40}$$

As a second approximation, we consider the system to be thermomechanically simple at the microscale. For such a system, the body source of entropy is equal to the energy source divided by the temperature. Additionally, the non-advective entropy flux is equal to the non-advective energy flux, consisting of heat flux and heat transfer due to mass dispersion, divided by the temperature. This approximation is stated

SEI Approximation 5.2 (Thermomechanically simple system) *For a microscopic thermomechanically simple system, the entropy source term is equal to the entity-based energy source divided by the temperature; and the entropy flux term is equal to the entity-based energy flux term divided by the temperature such that*

$$-b_\alpha + \frac{1}{\theta_\alpha} h_\alpha = 0 \tag{5.41}$$

and

$$\boldsymbol{\varphi}_\alpha - \frac{1}{\theta_\alpha}\left(\mathbf{q}_\alpha + \sum_{i\in\mathfrak{I}_s} \mu_{i\alpha}\rho_\alpha\omega_{i\alpha}\mathbf{u}_{i\alpha}\right) = \mathbf{0} \tag{5.42}$$

for entity α.

If a system is thermomechanically complex, the right sides of Eqs. (5.41) and (5.42) will not necessarily be zero, thus requiring some additional effort in obtaining closure equations. This situation will not be considered here. Thus the entropy inequality given by Eq. (5.40) simplifies by SEI Approximation 5.2 for phase w to

$$\frac{1}{\theta_w}\left(p_w\mathbf{l} + \mathbf{t}_w\right):\mathbf{d}_w - \frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_s} \rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left(\mu_{iw}|_{\theta_w} + \psi_{iw}\right)$$
$$-\left(\mathbf{q}_w + \sum_{i\in\mathfrak{I}_s} \overline{H}_{iw}\rho_w\omega_{iw}\mathbf{u}_{iw}\right)\cdot\nabla\left(\frac{1}{\theta_w}\right) - \frac{1}{\theta_w}\sum_{k\in\mathfrak{I}_{\mathrm{rxn}}} R_{kw}A_{kw} = \Lambda_w \geq 0\,. \tag{5.43}$$

5.5.2 Consideration of Equilibrium Conditions

Progress toward obtaining an SEI composed of a sum of products of forces and fluxes with each being zero at equilibrium can be assessed by considering the SEI obtained as compared to the desired form of Eq. (5.11). Equation (5.43) is composed of four terms, each of which is a product of two quantities. Note that the second and fourth terms involve summations over all species and all chemical reactions, respectively. The forces in each of the terms are, respectively, $\mathbf{d}_w$, $\nabla\left(\mu_{iw}|_{\theta_w} + \psi_{iw}\right)$, $\nabla(1/\theta_w)$, and A_{kw}. The first three of these independent variables have each been shown to be zero in the equilibrium analysis of Chap. 4. The affinity was defined such that it is zero at equilibrium. The multipliers of each of these forces is designated as a flux, and each of these fluxes must also be zero at equilibrium. Thus, Eq. (5.43) is an SEI for a multispecies, heat-conducting fluid in which diffusion and chemical reactions are occurring, subject to the two SEI Approximations being satisfied.[3] At the microscale, the development of this SEI from the CEI of Eq. (5.39) was straightforward. Later, in considering macroscale porous medium systems, it will be seen that additional assumptions will be needed to obtain a force-flux form for an SEI from a CEI.

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[3] By Eq. (2.25), only $N-1$ of the diffusive fluxes, $\mathbf{u}_{iw}$, are independent. This will be taken into account subsequently in Sect. 5.6.2 when developing closure relations.

5.6 Closure Relations

The utility of the SEI is in providing guidance for closure relations needed to make up for the deficit in the number of equations needed to specify the number of variables in those equations. Of course one could arbitrarily generate some additional closure relations and hope that they will reproduce the system physics, but proceeding in this manner would carry little chance of success. A more systematic approach makes use of the SEI. One should remember that regardless of what closure method is employed, the closure relations are only approximations that may be used to model some systems effectively but are typically appropriate for only a limited range of operating conditions. The process of closure introduces coefficients into the formulation that are dependent on material properties. From one perspective, closure may be seen as merely replacing one set of unknown variables with a different set of unknown coefficients. However, a successful closure process will result in coefficients that can be specified for a particular system whose dynamics can then be modeled. If a set of closure relations is not appropriate for a system, then these relations can be altered in light of system behavior, insights, and by relaxing assumptions that have been made. Closure relations are inherently different from general conservation equations which must not be violated in that they introduce approximations for insertion into those equations in an effort to make the equations solvable.

In light of this discussion, it is important to identify the number of equations available, the number of variables for which closure relations can be postulated from the SEI, and the number of additional relations that must be employed to completely close the problem description. We will address these issues in the next subsections for the single-phase system described in the preceding sections.

5.6.1 Count of Variables

For the case of a fluid phase, as we are modeling it, there are N species mass conservation equations ($\mathcal{M}_{*iw}$ from Table 2.1), three components of the vector momentum conservation equation ($\mathcal{P}_{*w}$ from Table 2.2), one energy equation ($\mathcal{E}_{*w}$ from Table 2.2), and the SEI in Eq. (5.43). Thus the total number of equations is $N+5$. The set of unknowns that arises in these equations, $\mathcal{V}$, is

$$\mathcal{V} = \{\rho_w, \omega_{iw}, \mathbf{v}_w, E_w, \Lambda_w, \psi_{iw}, \mathbf{g}_{iw}, h_w, K_{Ew}, \theta_w, \\ p_w, \mu_{iw}, \overline{H}_{iw}, r_{iw}, A_{kw}, \mathbf{t}_w, \mathbf{u}_{iw}, \mathbf{q}_w, R_{kw}\} \quad \text{for } i \in \mathfrak{I}_s, k \in \mathfrak{I}_{\mathrm{rxn}} \, . \qquad (5.44)$$

Note that each vector in Eq. (5.44) has three spatial components and the symmetric tensor $\mathbf{t}_w$ has six independent components. The quantities ψ_{iw} and $\overline{H}_{iw}$, as well as the components of $\mathbf{g}_{iw}$, all have N independent members, one for each species; $N-1$

independent values of ω_{iw}, $\mathbf{u}_{iw}$, μ_{iw}, and r_{iw} exist.[4] Additionally R_{kw} and A_{kw} each consist of N_{rxn} members. Thus, a total of $11N + 13 + 2N_{\text{rxn}}$ independent unknowns exist.

If we consider the conservation equations plus the SEI to account for the $N+5$ variables ρ_w, ω_{iw}, $\mathbf{v}_w$, E_w, and Λ_w, the deficit in equations is reduced to $10N + 8 + 2N_{\text{rxn}}$. The N body force potentials, ψ_{iw}, have to be specified for the problem; and the $3N$ components of $\mathbf{g}_{iw}$ are then obtained from Eq. (2.50). These $4N$ stipulations reduce the equation deficit to $6N + 8 + 2N_{\text{rxn}}$. The external body source of energy, h_w, is another quantity that must be specified for the system. Additionally, as has been discussed, the deviation kinetic energy, K_{Ew}, arises because the momentum and energy of the w phase are treated on a per entity basis. Such a treatment is appropriate only if K_{Ew} is negligible. Thus, we approximate it as zero. These two observations reduce the need for equations or conditions to $6N + 6 + 2N_{\text{rxn}}$.

Next, the thermodynamic framework is investigated to supply additional information. Equations for θ_w, p_w, and the $N-1$ independent values of μ_{iw} are obtained from the thermodynamic equations of state, Eqs. (3.48)–(3.50), respectively, applied to the w phase. However, a complication arises because these equations make use of the entropy per volume, η_w, which does not appear in the variables identified in $\mathcal{V}$. Fortunately, the Euler thermodynamic relation for E_w provided by Eq. (3.158) gives an additional constraint. Thus, these four relations reduce the count of unknowns in excess of equations by $N+1$. Also needed are relations for the N values of the partial mass enthalpy, $\overline{H}_{iw}$, which must be compiled as a function of p_w, θ_w, and composition according to the definition given in Eqs. (3.176) and (3.177). Thus, a total of $2N+1$ conditions are identified through thermodynamic relations, reducing the excess of variables to $4N + 5 + 2N_{\text{rxn}}$.

The $N-1$ independent values of r_{iw} are related to the chemical reactions R_{kw} by Eq. (5.36) when the molecular weights of the molecules and the stoichiometric coefficients of the reactions are known. Similarly, the N_{rxn} variables A_{kw} are accounted for by Eq. (5.37) applied to each species. Thus, the number of equations still needed is reduced to $3N + 6 + N_{\text{rxn}}$.

This equation deficit can be eliminated if expressions are found for the 6 independent members of $\mathbf{t}_w$, $3(N-1)$ members of $\mathbf{u}_{iw}$, 3 elements of $\mathbf{q}_w$, and the N_{rxn} independent reactions, R_{kw}. These variables are all fluxes found in the force-flux pairing of the SEI, Eq. (5.43). We reiterate that functional forms for these variables in terms of other system variables can be proposed based on experimental studies or other sources of insight. The SEI serves as a useful relation that provides guidance in the selection of the equations, and some of the results obtained are found to be good models of many systems.

In light of the fact that only $N-1$ vector values of $\mathbf{u}_{iw}$ and $N-1$ values of μ_{iw} are independent, only these values should appear in the SEI if closure is to be accomplished. In particular, the second force flux pair in Eq. (5.43) is of primary interest in determining the closure relation for the diffusive transport vector. In the following subsection, we will re-express this term.

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[4] Only $N-1$, rather than N, independent components of these quantities exist because of the constraints given by Eqs. (2.22), (2.25), (3.43), and (2.20), respectively.

5.6.2 Diffusive Flux Rearrangement

Only $N-1$ independent diffusive flux vectors exist because, based on Eq. (2.25), the Nth value can be calculated if the first $N-1$ are known according to

$$\sum_{i\in\mathfrak{I}_{s/N}} \omega_{iw}\mathbf{u}_{iw} = -\omega_{Nw}\mathbf{u}_{Nw} \, , \tag{5.45}$$

where $\mathfrak{I}_{s/N}$ indicates that the summation is over all species in $\mathfrak{I}_s$ except the Nth species. The diffusion term in Eq. (5.43) can be expanded to obtain

$$\sum_{i\in\mathfrak{I}_s} \rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left(\mu_{iw}|_{\theta_w} + \psi_{iw}\right) = \sum_{i\in\mathfrak{I}_{s/N}} \rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left(\mu_{iw}|_{\theta_w} + \psi_{iw}\right) + \rho_w\omega_{Nw}\mathbf{u}_{Nw}\cdot\nabla\left(\mu_{Nw}|_{\theta_w} + \psi_{Nw}\right) \, . \tag{5.46}$$

Substitution of Eq. (5.45) into this expansion to eliminate $\omega_{Nw}\mathbf{u}_{Nw}$ and collecting terms provides

$$\sum_{i\in\mathfrak{I}_s} \rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left(\mu_{iw}|_{\theta_w} + \psi_{iw}\right) = \sum_{i\in\mathfrak{I}_{s/N}} \rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left[\mu_{iw}|_{\theta_w} + \psi_{iw} - \left(\mu_{Nw}|_{\theta_w} + \psi_{Nw}\right)\right] \, . \tag{5.47}$$

The presence of the potentials of the Nth species as reference values suggests that the Nth species should be identified to be one that is present in significant amounts, such as the solvent. The right side of Eq. (5.47) is in independent force-flux form with both the diffusive fluxes and the gradients of potentials being zero at equilibrium. Substitution of Eq. (5.47) into Eq. (5.43) then yields the SEI

$$\frac{1}{\theta_w}\left(p_w\mathbf{I} + \mathbf{t}_w\right):\mathbf{d}_w - \frac{1}{\theta_w}\sum_{i\in\mathfrak{I}_{s/N}} \rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left[\mu_{iw}|_{\theta_w} + \psi_{iw} - \left(\mu_{Nw}|_{\theta_w} + \psi_{Nw}\right)\right] - \left(\mathbf{q}_w + \sum_{i\in\mathfrak{I}_s}\overline{H}_{iw}\rho_w\omega_{iw}\mathbf{u}_{iw}\right)\cdot\nabla\left(\frac{1}{\theta_w}\right) - \frac{1}{\theta_w}\sum_{k\in\mathfrak{I}_{\text{rxn}}} R_{kw}A_{kw} = \Lambda_w \geq 0 \, . \tag{5.48}$$

5.7 Special Cases

The SEI of Eq. (5.48) is a rather general form. There are some simpler single-phase systems for which the entropy generation rate can be described as a subset of this general form. Several of these will be listed here along with the restrictions that apply.

5.7.1 Single-species Phase

When the w fluid phase is composed of just a single species, the diffusive velocity is zero because the species velocity is trivially equal to the phase velocity. Additionally, no chemical reactions can be occurring since such reactions would have to produce another species from a reactant. Thus, Eq. (5.48) simplifies to

$$\frac{1}{\theta_w}\left(p_w\mathbf{l}+\mathbf{t}_w\right):\mathbf{d}_w-\mathbf{q}_w\cdot\nabla\left(\frac{1}{\theta_w}\right)=\Lambda_w\geq 0\,. \tag{5.49}$$

The terms that remain in this equation are responsible for entropy generation due to dissipative processes within the flow (i.e., viscous effects) and non-advective heat transport (i.e., conduction) within the phase.

5.7.2 Single-species, Isothermal Phase

If a phase is composed of a single species and is isothermal such that the temperature is uniform and no heat is being conducted, the SEI for a single phase reduces further to

$$\frac{1}{\theta_w}\left(p_w\mathbf{l}+\mathbf{t}_w\right):\mathbf{d}_w=\Lambda_w\geq 0\,. \tag{5.50}$$

This equation indicates that the entropy production can be accounted for by considering only viscous dissipation.

The two simplified cases considered here make study of the specific systems to which they apply easier than dealing with the full SEI of Eq. (5.48). They also demonstrate how knowledge of a general SEI, and its antecedent CEI, can serve as a starting point for development of the corresponding equations for a simpler system. Also, we note that the special cases considered can be developed as special instances of the general model for which coefficients in closure relations are zero. Thus a model can be simplified either at the level of formulation of an SEI or at a later stage, after the SEI has been used to obtain closure relations. We now turn to the analysis indicated in the lower right corner of Fig. 5.1, which involves use of the SEI to develop closure relations.

5.8 Conjugate Force-flux Closure

The SEI of Eq. (5.48), as well as the special cases of Eqs. (5.49) and (5.50), are forms of the EI that consist of a sum of force-flux pairs on the left side. This SEI was derived under various limiting conditions from the CEI and provides a statement of necessary conditions that must be satisfied by allowable forms of closure relations. At equilibrium, each member of a force and flux pair must equal zero. Away from equilibrium, the dissipative fluxes in the force-flux pairs produce entropy. Thus, we seek closure relations such that each independent flux is indeed zero at equilibrium and, when appearing in the SEI, will provide non-negative entropy production for all values of the independent forces. Forms of the closure relations that satisfy these conditions are not unique. In this subsection, we explore a simple family of closure relations based upon individual consideration of pairs of a flux and the force it multiplies, known as its conjugate force. More complicated closure approximations are possible, and an example of cross-coupled closure relations is given in Sect. 5.9.

5.8.1 Stress Tensor

Consider the first force-flux pair in Eq. (5.48). If we examine the entropy producing attributes of the stress tensor in isolation from other entropy producing processes, we consider the expression

$$\frac{1}{\theta_w}\left(p_w\mathbf{I}+\mathbf{t}_w\right):\mathbf{d}_w \geq 0\,. \tag{5.51}$$

We know that at equilibrium the force $\mathbf{d}_w = \mathbf{0}$. The flux multiplying this force must also be zero at equilibrium so that at equilibrium

$$\mathbf{t}_w = -p_w\mathbf{I}\,. \tag{5.52}$$

This condition states that the static part of the stress tensor is due to fluid pressure and is isotropic in form. Away from equilibrium, we can write

$$\mathbf{t}_w = -p_w\mathbf{I} + \boldsymbol{\tau}_w\,, \tag{5.53}$$

where $\boldsymbol{\tau}_w = \mathbf{0}$ at equilibrium. In this expression, we assume that the dynamic aspects of the system do not impact the fact that p_w is a thermodynamic variable defined at equilibrium (i.e., a local equilibrium assumption is applied) and $\boldsymbol{\tau}_w$ is termed the viscous stress tensor, since it is the dissipative part of the stress tensor that accounts for entropy production.

Equations (5.51) and (5.53) can be combined to write

$$\frac{1}{\theta_w}\boldsymbol{\tau}_w:\mathbf{d}_w \geq 0\,, \tag{5.54}$$

or, since temperature is positive,

$$\boldsymbol{\tau}_w:\mathbf{d}_w \geq 0\,. \tag{5.55}$$

Thus, the closure problem for the stress tensor is reduced to determining the functional form of the symmetric viscous stress tensor, $\boldsymbol{\tau}_w$, that satisfies Eq. (5.55) regardless of the value of $\mathbf{d}_w$, is zero at equilibrium, and provides a useful description of at least some physical systems.

The mathematical aspects of this problem can be approached by assuming $\boldsymbol{\tau}_w$ is a function of $\mathbf{d}_w$ such that $\boldsymbol{\tau}_w = \mathbf{0}$ when $\mathbf{d}_w = \mathbf{0}$. A Taylor series expansion around this equilibrium state then gives

$$\boldsymbol{\tau}_w(\mathbf{d}_w) = \boldsymbol{\tau}_w(\mathbf{0}) + \left.\frac{\partial \boldsymbol{\tau}_w}{\partial \mathbf{d}_w}\right|_{\mathbf{d}_w=\mathbf{d}_w^*} : \mathbf{d}_w \,, \tag{5.56}$$

where $\mathbf{d}_w^*$ is the value of $\mathbf{d}_w$ for which the identity is satisfied. Because $\boldsymbol{\tau}_w(\mathbf{0}) = \mathbf{0}$, this equation may also be written

$$\boldsymbol{\tau}_w = \hat{\mathbf{a}}_w : \mathbf{d}_w \,, \tag{5.57}$$

where $\hat{\mathbf{a}}_w$ is a fourth order tensor. In the best of circumstances, $\hat{\mathbf{a}}_w$ will be a constant tensor for the system, meaning that the indicated linear dependence of $\boldsymbol{\tau}_w$ on $\mathbf{d}_w$ is a good model. If the fluid is taken to be isotropic, the equality given by Eq. (5.57) must be invariant with respect to rotations of the coordinate system. This stipulation imposes the restriction that for the w phase of interest, $\hat{\mathbf{a}}_w$ must be isotropic. It can be shown that an isotropic fourth order tensor may be written in terms of three parameters so that Eq. (5.57) may be greatly reduced to [5]

$$\boldsymbol{\tau}_w = \hat{a}_1 \mathbf{d}_w + \hat{a}_2 \mathbf{d}_w^{\mathrm{T}} + \hat{a}_3 \mathbf{I}\mathbf{I} : \mathbf{d}_w \,. \tag{5.58}$$

Because $\mathbf{d}_w$ is symmetric, $\mathbf{d}_w = \mathbf{d}_w^{\mathrm{T}}$, and Eq. (5.58) simplifies to

$$\boldsymbol{\tau}_w = 2\hat{\mu}_w \mathbf{d}_w + \hat{a}_3 \mathbf{I}\mathbf{I} : \mathbf{d}_w \,, \tag{5.59}$$

where $2\hat{\mu}_w = \hat{a}_1 + \hat{a}_2$ such that now only two parameters need to be determined, $\hat{a}_3$ and $\hat{\mu}_w$. It is common practice to calculate the trace of $\boldsymbol{\tau}_w$, which is

$$\mathbf{I} : \boldsymbol{\tau}_w = (2\hat{\mu}_w + 3\hat{a}_3)\, \mathbf{I} : \mathbf{d}_w \,. \tag{5.60}$$

Rather than seeking a value for $\hat{a}_3$, we define $3\hat{\kappa}_w = 2\hat{\mu}_w + 3\hat{a}_3$ and let $\hat{\mu}_w$ and $\hat{\kappa}_w$ be the two unknown parameters. This gives the final form of $\boldsymbol{\tau}_w$ as

$$\boldsymbol{\tau}_w = 2\hat{\mu}_w \mathbf{d}_w + \left(\hat{\kappa}_w - \frac{2}{3}\hat{\mu}_w\right) \mathbf{I}\mathbf{I} : \mathbf{d}_w \,. \tag{5.61}$$

In this expression, $\hat{\mu}_w$ is called the dynamic viscosity and $\hat{\kappa}_w$ is the bulk viscosity. The bulk viscosity is only important at locations where rapid expansion or compression of a fluid occurs, such as that due to shock waves. It provides a measure of the difference between the mechanical pressure in a dynamic system and the thermodynamic pressure and thus, in essence, extends the range of applicability of the

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[5] The condition of isotropy of a fourth order tensor is most easily written in indicial notation as $\hat{a}_{ijkl} = \hat{a}_1 \delta_{ik}\delta_{jl} + \hat{a}_2 \delta_{il}\delta_{jk} + \hat{a}_3 \delta_{ij}\delta_{kl}$ where δ_{ij} is a Kronecker delta. With $\mathbf{d}_w$ written in indicial form as d_{jk}, Eq. (5.58) is then obtained using vector notation.

local equilibrium assumption in studying a system undergoing rapid compression or expansion. The bulk viscosity is often neglected and is not needed when the flow occurs with $\mathsf{I}{:}\mathbf{d}_w = 0$.

Substitution of Eq. (5.61) into Eq. (5.55) provides the condition

$$\boldsymbol{\tau}_w{:}\mathbf{d}_w = 2\hat{\mu}_w \mathbf{d}_w{:}\mathbf{d}_w + \left(\hat{\kappa}_w - \frac{2}{3}\hat{\mu}_w \right) (\mathsf{I}{:}\mathbf{d}_w)^2 \geq 0 \, . \tag{5.62}$$

In this equation, $\mathbf{d}_w{:}\mathbf{d}_w$ is a non-negative quantity, as is $(\mathsf{I}{:}\mathbf{d}_w)^2$. It is easy to see that Eq. (5.62) is always satisfied if the dynamic and bulk viscosities are non-negative. The question that remains worth considering is whether $\boldsymbol{\tau}_w$, as proposed in Eq. (5.61), actually describes the viscous behavior of any fluids such that the general total stress, as defined by Eq. (5.53), can be written for those cases as

$$\mathbf{t}_w = -p_w \mathsf{I} + 2\hat{\mu}_w \mathbf{d}_w + \left(\hat{\kappa}_w - \frac{2}{3}\hat{\mu}_w \right) \mathsf{II}{:}\mathbf{d}_w \, . \tag{5.63}$$

Fluids that do obey Eq. (5.63) indeed exist and are referred to as Newtonian fluids. If a Newtonian fluid fills the gap between two solid, horizontal, parallel planes, lateral translation of one plane will result in the fluid at each plane surface moving at the velocity of the surface with the velocity profile changing linearly between the two surfaces. The greater the viscosity, which is a measure of internal friction in the fluid, the greater the force that is needed to cause one plane to translate while holding the other fixed. For a Newtonian fluid, the force required to translate one plate is proportional to the area of the plates and the velocity of translation; the force is inversely proportional to the distance between the plates. The dynamic viscosity is the coefficient of proportionality. Newtonian behavior has been found to be common for many small molecular weight fluids, such as water, air, and simple alcohols. More complex fluids, such as ketchup, paint, blood, and large molecular weight polymers, are non-Newtonian.

The extension of the concept of Newtonian behavior of a fluid to multiple dimensions leads to the expression for the stress tensor given by Eq. (5.63). A key issue in determining the utility of this relation is whether the coefficients $\hat{\mu}_w$ and $\hat{\kappa}_w$ are constant, or nearly constant, for a particular fluid over a range of laminar flow operating conditions. A closure analysis that leads to coefficients with a high level of unexplainable variability for a particular system most likely indicates that some of the physics of the problem is not being accounted for correctly, but is being buried in the coefficients. The fact that the relatively simple Newtonian expression, obtained from a linear analysis, does not universally describe fluid behavior should not be surprising. Perhaps what is surprising is the fact that many fluids are indeed modeled well by this simple equation.

Substitution of Eq. (5.63) into the momentum equation $\mathcal{P}_{*w}$ constructed from Table 2.2 gives

$$\frac{\mathrm{D}_w(\rho_w\mathbf{v}_w)}{\mathrm{D}t}+\rho_w\mathbf{v}_w\mathbf{l}{:}\mathbf{d}_w-\rho_w\mathbf{g}_w+\nabla p_w-\nabla\cdot\left[2\hat{\mu}_w\mathbf{d}_w+\left(\hat{\kappa}_w-\frac{2}{3}\hat{\mu}_w\right)\mathbf{ll}{:}\mathbf{d}_w\right]=\mathbf{0}\,. \tag{5.64}$$

Consider the special case when the fluid is incompressible. This condition is imposed by requiring that $\mathrm{D}_w\rho_w/\mathrm{D}t = 0$, which means that, although the density of the fluid in a system need not be uniform, the density of a fluid particle remains unchanged as it moves through the system. Based on mass conservation equation $\mathcal{M}_{*w}$, Eq. (2.19), the incompressibility condition implies that $\mathbf{l}{:}\mathbf{d}_w = 0$. If $\hat{\mu}_w$ is constant, these conditions reduce Eq. (5.64) directly to

$$\rho_w\frac{\mathrm{D}_w\mathbf{v}_w}{\mathrm{D}t}-\rho_w\mathbf{g}_w+\nabla p_w-2\hat{\mu}_w\nabla\cdot\mathbf{d}_w=\mathbf{0}\,. \tag{5.65}$$

From the rate of strain tensor defined as in Eq. (2.16), we obtain

$$\nabla\cdot\mathbf{d}_w=\frac{1}{2}\nabla\cdot\left[\nabla\mathbf{v}_w+(\nabla\mathbf{v}_w)^{\mathrm{T}}\right]=\frac{1}{2}\left[\nabla^2\mathbf{v}_w+\nabla(\nabla\cdot\mathbf{v}_w)\right]\,. \tag{5.66}$$

However, $\nabla\cdot\mathbf{v}_w = \mathbf{l}{:}\mathbf{d}_w$ so that the second term in the bracket is zero. Substitution of Eq. (5.66) back into Eq. (5.65) then gives

$$\rho_w\frac{\mathrm{D}_w\mathbf{v}_w}{\mathrm{D}t}-\rho_w\mathbf{g}_w+\nabla p_w-\hat{\mu}_w\nabla^2\mathbf{v}_w=\mathbf{0}\,. \tag{5.67}$$

Equation (5.67) is the Navier-Stokes equation for an incompressible, Newtonian fluid with a constant viscosity. More complex equations encountered along the way in simplifying the general momentum equation to this form are sometimes also referred to as the Navier-Stokes equation.

The closure procedure employed here has provided an approximation for the six independent elements of the symmetric tensor, $\mathbf{t}_w$. If we are interested in a single-species, isothermal phase, no additional closure relations are needed (i.e., no diffusion velocities or reactions and no non-advective heat flux). Thus the full equation set would be closed; and the system is solvable, subject to specification of boundary conditions.

5.8.2 Diffusion Vector

Now let us turn to the second force-flux pair in Eq. (5.48). Consideration of this term in isolation from other processes gives the conjugate relation

$$-\sum_{i\in\mathfrak{I}_{s/N}}\rho_w\omega_{iw}\mathbf{u}_{iw}\cdot\nabla\left[\mu_{iw}|_{\theta_w}+\psi_{iw}-\left(\mu_{Nw}|_{\theta_w}+\psi_{Nw}\right)\right]\geq 0\,. \tag{5.68}$$

Linearization of the dependence of the flux on only its conjugate force yields

$$\mathbf{u}_{iw}=-\hat{\mathbf{D}}_{iw}\cdot\nabla\left[\mu_{iw}|_{\theta_w}+\psi_{iw}-\left(\mu_{Nw}|_{\theta_w}+\psi_{Nw}\right)\right]\quad\text{for } i\in\mathfrak{I}_{s/N}\,. \tag{5.69}$$

The negative sign is employed so that if this expression is substituted back into Eq. (5.68), the entropy generation will be positive when $\hat{\mathsf{D}}_{iw}$ is positive semi-definite. The fluid is considered to be isotropic, and the only isotropic tensor is the scaled unit tensor. Therefore, for an isotropic fluid,

$$\hat{\mathsf{D}}_{iw} = \hat{D}_{iw}\mathsf{I}\ . \tag{5.70}$$

With this minor modification, that nevertheless reduces the number of parameter values that must be determined, the diffusion expression becomes

$$\mathbf{u}_{iw} = -\hat{D}_{iw}\nabla\left[\mu_{iw}|_{\theta_w} + \psi_{iw} - \left(\mu_{Nw}|_{\theta_w} + \psi_{Nw}\right)\right] \quad \text{for } i \in \mathfrak{I}_{s/N}\ . \tag{5.71}$$

Equation (5.71) applies to each of the $N-1$ species in a multispecies system while the diffusion expression for the Nth species is obtained from Eq. (5.45). The use of only the conjugate force limits the applicability of this diffusion expression to cases where the diffusing chemical species are present in low enough concentrations that their interaction with each other is unimportant in comparison to their interactions with the Nth species, the solvent.

We observe, additionally, that if the only body force that acts on the system is gravity,

$$\psi_{iw} = \psi_w \quad \text{for } i \in \mathfrak{I}_s\ . \tag{5.72}$$

In this common case, closure relation Eq. (5.71) simplifies to

$$\mathbf{u}_{iw} = -\hat{D}_{iw}\nabla\left(\mu_{iw}|_{\theta_w} - \mu_{Nw}|_{\theta_w}\right) \quad \text{for } i \in \mathfrak{I}_{s/N}\ . \tag{5.73}$$

5.8.3 Non-advective Heat Flux

Next consider the third term from Eq. (5.48) as an isolated entropy producing process. This leads to an expression for entropy generation,

$$-\left(\mathbf{q}_w + \sum_{i\in\mathfrak{I}_s} \overline{H}_{iw}\rho_w\omega_{iw}\mathbf{u}_{iw}\right)\cdot\nabla\left(\frac{1}{\theta_w}\right) \geq 0\ . \tag{5.74}$$

This expression quantifies the entropy generated by heat conduction and the transport of enthalpy that accompanies diffusion. Linearization of this expression around the equilibrium state for the conjugate force gives

$$\mathbf{q}_w + \sum_{i\in\mathfrak{I}_s} \overline{H}_{iw}\rho_w\omega_{iw}\mathbf{u}_{iw} = -\hat{\mathsf{k}}_{\theta w}\cdot\nabla\left(\frac{1}{\theta_w}\right)\ . \tag{5.75}$$

Because of fluid isotropy, the tensor of proportionality, $\hat{\mathsf{k}}_{\theta w}$, is a non-negative scalar multiplied by the unit tensor so that

$$\mathbf{q}_w = -\hat{k}_{\theta w} \nabla \left(\frac{1}{\theta_w} \right) - \sum_{i \in \mathfrak{I}_s} \overline{H}_{iw} \rho_w \omega_{iw} \mathbf{u}_{iw} \, . \tag{5.76}$$

Application of the product rule to the gradient term yields the alternative representation,

$$\mathbf{q}_w = \frac{\hat{k}_{\theta w}}{\theta_w^2} \nabla \theta_w - \sum_{i \in \mathfrak{I}_s} \overline{H}_{iw} \rho_w \omega_{iw} \mathbf{u}_{iw} \, . \tag{5.77}$$

When interdiffusion is negligible, or if the fluid is composed of only one species, Eq. (5.77) reduces to the expression known as Fourier's law where the non-advective heat transfer is proportional to the temperature gradient. Note that in our expression of this law, no minus sign appears because of the sign convention chosen for $\mathbf{q}_w$ in the energy equation such that it provides a source of energy at a point rather than a sink. Also, it has been found experimentally that $\hat{k}_{\theta w}$ tends to be proportional to θ_w^2 so that $\hat{k}_{\theta w}/\theta_w^2$ in Eq. (5.77) has small variation over a significant range of temperature.

5.8.4 *Chemical Reaction*

The last force-flux pair in Eq. (5.48) accounts for entropy production due to chemical reactions. In isolation from other processes, this term provides the entropy generation condition

$$-\sum_{k \in \mathfrak{I}_{\text{rxn}}} R_{kw} A_{kw} \geq 0 \, . \tag{5.78}$$

In turn, this suggests the linearized expression for each reaction of the form

$$R_{kw} = -\hat{K}_{\text{rxn}k} A_{kw} \quad \text{for } k \in \mathfrak{I}_{\text{rxn}} \, . \tag{5.79}$$

Although this expression provides a description of the chemical reaction rate in terms of the affinity, this form is rarely used in practice. Instead, chemical reaction rates are typically determined via laboratory experiments, or subscale theory, yielding an expression for rates in terms of concentrations of reactants. Because this approach to determining reaction pathways and rates is more accurate and general than a linearization approach, experimentally or mechanistically based expressions are used in modeling. Discussions of relations between reaction rates and affinities may be found in the literature [e.g., 5, 6].

5.9 Cross-coupled Closure

The conjugate closure relations given in Sect. 5.8 represent the simplest set of conditions that are consistent with the entropy inequality and with experimental observations that conjugate pairs are of leading order importance. Because of these features, this simple approach to obtaining closure relations is often used in developing mechanistic models of transport phenomena at the microscale. The derivations of the Navier-Stokes equation and of Fourier's law of heat conduction are classical examples of the applicability and utility of the results of conjugate closure. However, this is not the full story.

Careful experimental observations have shown that fluxes can be caused by forces other than the conjugate force alone. For example, species diffusion can result from a temperature gradient; this is known as the Soret effect. Similarly, non-advective heat transport can be caused by a gradient in chemical potential; this is known as the Dufour effect. Diffusion of each chemical species can be influenced by the diffusion of all the other chemical species present. These cross-coupled mechanisms illustrate symmetries collectively referred to as the Onsager reciprocal relations [8, 9]. The bases for these symmetries is rooted in the consequences of molecular reversal and its manifestation at the microscale. Kinetic theory can be used to prove these symmetries.

A second observation regarding coupled symmetries was made by Nobel Laureate Ilya Prigogine regarding the nature of the forces and fluxes that admit cross coupling [6, 11]. This observation is based on the Curie symmetry principle [13]; roughly speaking, it restricts coupled phenomena to be of similar character. For example, for isotropic systems a force may not be coupled with fluxes whose ranks differ from that of the force by an odd number [1, 7, 10]. Scalar forces, such as affinities, have greater symmetry than anisotropic forces such as gradients in chemical and gravitational potential, so these effects cannot be coupled. Similarly, tensor forces cannot be coupled with vector forces. The net result of the symmetry principle is a restriction on the form of cross-coupled approximations.

One last observation is needed regarding cross-coupled closure methods. For systems involving directional forces such as a magnetic field, the normal form of the Onsager reciprocal relations, which generalize the dependence of fluxes on forces in addition to the conjugate forces when local equilibrium may be presumed, does not apply. Since we are not considering electromagnetic fields in this work, this complication will not be relevant to our discussion, but should be kept in mind for those wishing to extend TCAT methods to more complex systems.

The generalization of the dependence of each of the four fluxes on the forces in SEI Eq. (5.48) can be expressed as the dependence of each flux on the full set of forces, requiring that the flux be zero at equilibrium, and performing a Taylor series expansion around the equilibrium state for all of the forces for each flux. The results for the fluxes in Eq. (5.48) are

$$\boldsymbol{\tau}_w = \hat{\mathbf{a}}^{(4)}_{\tau d}:\mathbf{d}_w - \sum_{k\in\mathfrak{I}_{s/N}} \hat{\mathbf{a}}^{(3)}_{k\tau f}\cdot\mathbf{f}_{kw} - \hat{\mathbf{a}}^{(3)}_{\tau\theta}\cdot\nabla\left(\frac{1}{\theta_w}\right) - \sum_{k\in\mathfrak{I}_{\mathrm{rxn}}} \hat{\mathbf{a}}^{(2)}_{k\tau A} A_{kw}\,, \tag{5.80}$$

$$\mathbf{u}_{iw} = \hat{\mathbf{a}}^{(3)}_{iud}:\mathbf{d}_w - \sum_{k\in\mathfrak{I}_{s/N}} \hat{\mathbf{a}}^{(2)}_{ikuf}\cdot\mathbf{f}_{kw} - \hat{\mathbf{a}}^{(2)}_{iu\theta}\cdot\nabla\left(\frac{1}{\theta_w}\right) - \sum_{k\in\mathfrak{I}_{\mathrm{rxn}}} \hat{\mathbf{a}}^{(1)}_{ikuA} A_{kw}$$

$$\text{for } i \in \mathfrak{I}_{s/N} \,, \tag{5.81}$$

$$\begin{aligned}\mathbf{q}_w + \sum_{k \in \mathfrak{I}_s} \overline{H}_{kw} \rho_w \omega_{kw} \mathbf{u}_{kw} =& \hat{\mathbf{a}}^{(3)}_{qd} : \mathbf{d}_w - \sum_{k \in \mathfrak{I}_{s/N}} \hat{\mathbf{a}}^{(2)}_{kqf} \cdot \mathbf{f}_{kw} - \hat{\mathbf{a}}^{(2)}_{q\theta} \cdot \nabla \left(\frac{1}{\theta_w} \right) \\ & - \sum_{k \in \mathfrak{I}_{\text{rxn}}} \hat{\mathbf{a}}^{(1)}_{kqA} A_{kw} \,, \end{aligned} \tag{5.82}$$

and

$$R_{iw} = \hat{\mathbf{a}}^{(2)}_{iRd} : \mathbf{d}_w - \sum_{k \in \mathfrak{I}_{s/N}} \hat{\mathbf{a}}^{(1)}_{ikRf} \cdot \mathbf{f}_{kw} - \hat{\mathbf{a}}^{(1)}_{iR\theta} \cdot \nabla \left(\frac{1}{\theta_w} \right) - \sum_{k \in \mathfrak{I}_{\text{rxn}}} \hat{\mathbf{a}}^{(0)}_{ikRA} A_{kw} \quad \text{for } i \in \mathfrak{I}_{\text{rxn}} \,. \tag{5.83}$$

A superscript in parentheses indicates the order of the coefficient tensor, and $\mathbf{f}_{kw}$ is used as a shorthand notation with

$$\mathbf{f}_{kw} = \nabla \left[\mu_{kw}|_{\theta_w} + \psi_{kw} - \left(\mu_{Nw}|_{\theta_w} + \psi_{Nw} \right) \right] \tag{5.84}$$

when ψ_{kw} is species dependent, or in simplified form as

$$\mathbf{f}_{kw} = \nabla \left(\mu_{kw}|_{\theta_w} - \mu_{Nw}|_{\theta_w} \right) \tag{5.85}$$

when Eq. (5.72) applies.

We are studying an isotropic system. No isotropic first- or third-order tensors exist, so these coefficient tensors are zero. The procedure for handling an isotropic fourth-order tensor has been demonstrated in the previous section. The only second-order isotropic tensor is a scalar multiplying the unit tensor. Thus, Eqs. (5.80)–(5.83) simplify, respectively, to

$$\boldsymbol{\tau}_w = 2\hat{\mu}_w \mathbf{d}_w + \left(\hat{\kappa}_w - \frac{2}{3} \hat{\mu}_w \right) \mathbf{I}\mathbf{I} : \mathbf{d}_w - \sum_{k \in \mathfrak{I}_{\text{rxn}}} \hat{a}_{k\tau A} \mathbf{I} A_{kw} \,, \tag{5.86}$$

$$\mathbf{u}_{iw} = - \sum_{k \in \mathfrak{I}_{s/N}} \hat{a}_{ikuf} \mathbf{f}_{kw} - \hat{a}_{iu\theta} \nabla \left(\frac{1}{\theta_w} \right) \quad \text{for } i \in \mathfrak{I}_{s/N} \,, \tag{5.87}$$

$$\mathbf{q}_w + \sum_{k \in \mathfrak{I}_s} \overline{H}_{kw} \rho_w \omega_{kw} \mathbf{u}_{kw} = - \sum_{k \in \mathfrak{I}_{s/N}} \hat{a}_{kqf} \mathbf{f}_{kw} - \hat{a}_{q\theta} \nabla \left(\frac{1}{\theta_w} \right) \,, \tag{5.88}$$

and

$$R_{iw} = \hat{a}_{iRd} \mathbf{I} : \mathbf{d}_w - \sum_{k \in \mathfrak{I}_{\text{rxn}}} \hat{a}_{ikRA} A_{kw} \quad \text{for } i \in \mathfrak{I}_{\text{rxn}} \,. \tag{5.89}$$

Recall that according to the symmetry principle, fluxes should not depend on forces of a rank that differs by an odd number. The last terms in Eq. (5.86) and the first term in Eq. (5.89) involve forces that differ from the order of their fluxes by 2. Thus the effective force contributions of these terms are allowable. Equations (5.87) and (5.88) exhibit the cross-coupling of mass diffusion due to non-advective heat transfer (Soret effect) and heat transfer due to diffusive mass transfer (Dufour effect), respectively. Not to be overlooked is the cross coupling that is indicated for diffusive transfer of species *i* due to gradients in potentials of the other chemical species present. This force is not accounted for if only conjugate forces are considered.

The issue of the magnitudes of the various coefficients that appear in Eqs. (5.86)–(5.89) is, for the most part, beyond the scope of what we wish to consider here. We will note that the conjugate force-flux relation is the dominant one. Additionally, when the constitutive forms are substituted back into SEI Eq. (5.48), the coefficient values must be such that violation of this inequality principle is not possible. We observe that the set of closure relations listed provides the $3N+6+N_{\mathrm{rxn}}$ additional equations needed such that the equation system is solvable. However, this good news should not obscure the fact that the unknown fluxes have been obtained as functions of the forces at a cost of $1+2N+2N_{\mathrm{rxn}}+(N-1)^2+(N_{\mathrm{rxn}}-1)^2$ parameters that must be specified. This trade is worthwhile if the parameters can be determined to be essentially material parameters that do not depend on the processes in the system. When the parameters associated with cross-coupling can all be set to zero, the unknown parameter set is reduced to $2+N+N_{\mathrm{rxn}}$ members. Extensive discussion of the symmetry principle, Onsager's theory, and bounds and properties of the parameters can be found in the literature [e.g., 1, 3, 5, 8, 10, 12].

5.10 Summary

In this chapter, we have illustrated how closure relations for a microscale system can be derived based upon a constrained statement of the second law of thermodynamics. The analysis followed the steps indicated in Fig. 5.1. The components of this analysis included the entropy inequality augmented by Lagrange multipliers acting on conservation and balance equations, thermodynamic principles, and equilibrium conditions. These components were derived in previous chapters. To enable the analysis to lead to an expression for the entropy generation rate due to irreversible processes in terms of force-flux pairs, Lagrange multipliers were chosen to eliminate material derivatives. The result of this analysis led to a constrained entropy inequality, which did not involve application of any approximations to the initial set of equations. The general CEI can serve as a starting point for analyses of systems other than those considered here. Approximations were employed to arrive at a strict force-flux form of the entropy inequality, which was referred to as the simplified entropy inequality (SEI). The SEI provides guidance to the selection of closure relations needed to account for a deficit in equations needed to solve for the system unknowns. The SEI was used to derive closure relations involving the linearized relations between forces and fluxes. It was shown that even these linear forms provide expressions that have been shown to be useful in modeling systems (e.g., Newtonian stress tensor, Navier-Stokes equation, Fourier heat flux, Soret and

Dufour effects). The closure relations provide a hierarchy of parameterized models in that simpler systems can be modeled as special cases (i.e., an isothermal system, a single-species phase, non-reacting fluid).

The only element of Fig. 5.1 that was not given attention here is the lower left corner involving subscale modeling and applications. Indeed, the focus of this chapter was on a theoretical approach to closure. Once closure is completed, two important issues arise. First, one must ascertain if any real physical systems behave in accord with the derived approximate equations. If no systems are found or if a system of interest does not behave according to the equations developed, the closure approach must be reassessed and modified with restrictions relaxed. Second, if systems exist that behave according to the physics described by the model, the parameters in the model must still be evaluated for the system of interest. For example, values of the dynamic viscosity, $\hat{\mu}_\alpha$, have been tabulated for a large number of fluids over a range of temperatures. These are obtained from experimental measurements on model systems and from methods for calculating fluid properties. This kind of support is essential to ensuring that the equations developed are applicable. For chemical reactions, mechanistic models that have been developed are superior to simply modeling a reaction as being proportional to the affinity.

The procedure detailed in this chapter is applicable to microscale systems in general. All elements of the closure procedure also have parallels for the larger scale TCAT models to be derived in subsequent chapters. Focusing on the relatively simple single-fluid-phase system afforded the opportunity to introduce important elements of the TCAT approach without the complexity that will accompany multiphase systems. A comparison of Fig. 5.1 with Fig. 1.3 provides an indication of the additional steps that are needed if a model is to be formulated at the macroscale rather than at the microscale. The elements of the tools needed to transform equations to a larger scale, as needed for TCAT analysis of a porous medium system, are the subject of the next chapter.

Exercises

5.1. Prove that an alternative form for the diffusion force-flux pair is

$$\begin{aligned}
&\sum_{i\in\mathfrak{I}_s} \rho_w \omega_{iw} \mathbf{u}_{iw}\cdot\nabla\left[\mu_{iw}|_{\theta_w} + \psi_{iw} - \left(\mu_{Nw}|_{\theta_w} + \psi_{Nw}\right)\right] \\
&\qquad = \sum_{i\in\mathfrak{I}_{s/N}} \rho_w \omega_{iw} \mathbf{u}_{iw}\cdot\left[\nabla\left(\mu_{iw}|_{\theta_w} + \psi_{iw}\right) + \sum_{k\in\mathfrak{I}_{s/N}} \frac{\omega_{kw}}{\omega_{Nw}}\nabla\left(\mu_{kw}|_{\theta_w} + \psi_{kw}\right)\right. \\
&\qquad \left. - \frac{1}{\rho_w\omega_{Nw}}\left(\nabla p_w + \sum_{k\in\mathfrak{I}_s} \rho_w \omega_{kw}\nabla\psi_{kw}\right)\right]. \qquad (5.90)
\end{aligned}$$

5.2. Show that if the mechanical pressure, $p_{w\mathrm{mech}}$ is the average normal stress such that $p_{w\mathrm{mech}} = -\mathbf{t}_w{:}\mathsf{I}/3$, then for a single component fluid

$$p_{w\mathrm{mech}} = p_w + \frac{\hat{\kappa}_w}{\rho_w}\frac{\mathrm{D}_w\rho_w}{\mathrm{D}t} ,$$

confirming that bulk viscosity is important when fast rates of density change contribute to a normal stress in excess of the thermodynamic pressure.

5.3. Consider a single-phase, single-species, isothermal, elastic solid. Develop the closed form of the stress tensor for this system.

5.4. For a single-species phase, the SEI is given by Eq. (5.49). Make a count of variables and equations that shows whether or not any additional equations will be needed to obtain a closed system description.

5.5. For a fluid phase w composed of two chemical species, A and B, show that $\mathbf{f}_{Aw}$ given in Eq. (5.84) may be written as

$$\mathbf{f}_{Aw} = \nabla\left(\mu_{Aw}|_{\theta_w} + \psi_{Aw}\right) - \nabla\left(\mu_{Bw}|_{\theta_w} + \psi_{Bw}\right) ;$$

and obtain the expression for $\mathbf{f}_{Bw}$.

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Chapter 6
Macroscale Conservation Principles

6.1 Overview

In the preceding chapter, we demonstrated how the elements of the TCAT approach, as depicted in Fig. 5.1, are used to obtain a closed set of microscale equations. The procedure for the development of macroscale equations is similar. However, an additional step is required to transform the microscale relations to the macroscale prior to applying the closure procedure. Fig. 6.1 highlights the elements that are needed to transform the conservation and balance equations to the macroscale.

Figure 6.1 indicates that to achieve a change in scale, averaging theorems are needed. These theorems facilitate a rigorous and systematic procedure for achieving the change in scale of the microscopic equations. Because volume, interface, common curve and common point entities all can arise in multiphase systems, families of theorems are needed for each of these entity classes. For completeness, the theorems are derived in detail in Appendix B. However, the main objective here is to employ the theorems as available tools for the development of TCAT models. Thus, mastery of the use of the theorems, rather than of their formulation, is the point of emphasis consistent with the approach of Fig. 6.1.

Recall that the macroscale is an averaged scale where conditions at a point are expressed in terms of averages of microscale conditions in some neighborhood of that point. This neighborhood is called the representative elementary volume (REV). Whereas the microscale perspective sees phases, interfaces, and common curves as juxtaposed entities, the averaging process gives rise to a representation of the system whereby phases each occupy a fraction of the volume associated with the REV. In addition, measures of interfacial area, common curve length, and the number of common points per volume arise. These entity densities do not exist at the microscale, but are a byproduct of the increase in length scale. An essential feature, however, is that if details are known at the microscale, averaging of certain aspects of these microscale details must result in macroscale quantities that are well-defined in terms of the microscopic precursors. This interscale consistency provides a link between the microscale and the macroscale that is important in model development,

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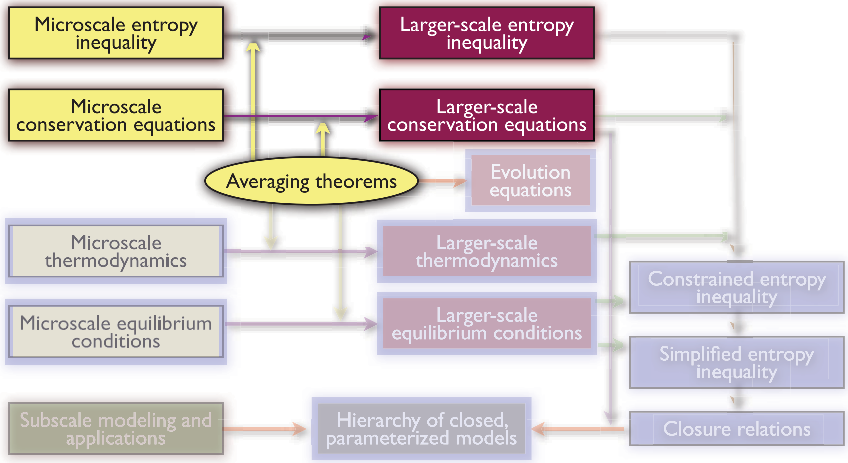

Fig. 6.1 TCAT elements of interest in Chap. 6 (after [6])

closure, and validation. The ability to include interface, common curve, and common point equations at the macroscale is a quality of TCAT model formulation that is important for proper accounting of microscale physics using macroscale equations. The absence of these interface and common curve macroscale equations in traditional modeling approaches is a major shortcoming that impedes the formulation of mechanistic, physics-based closure approximations. In some cases, this absence means that the equations employed for modeling are incomplete; in other cases, the absence means that the assumptions inherent in the model employed are unknown.

The set of equations to be averaged here includes mass, momentum, and energy conservation plus entropy balances. These equations are obtained for species in an entity and for the entity as a whole. They are formulated for phases, interfaces, and common curves[1]. If one is to model the full set of conservation equations for each chemical species in each entity of the system, the size of the set of equations to be employed increases rapidly as the number of phases and species increases. The formulation of the actual set of equations can be handled by making some simplifications. One must make decisions about tradeoff between simplicity and accuracy, about detailed and general parameterization, and about computational requirements to solve the equation set. In this chapter, we will develop the species-based conservation and balance equations as well as equations that apply to an entity as a whole.

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[1] Conservation and entropy balance equations at the microscale for a common point have been provided in Sect. 2.6, and the averaging theorem for these equations is obtained in Appendix B as Eq. (B.73) for completeness. However, subsequent focus is on systems with three phases or fewer that do not have common points. It will be seen, nonetheless, that because of the similarity of the forms of the equations, the inclusion of common point equations follows directly. Parameterization of these equations provides challenges in a case where common point physics impacts system behavior.

In subsequent applications, we will make use of combinations of these equations. A similar approach was used in the microscale fluid phase example of Chap. 5, where closure relations were obtained treating the mass conservation of each species separately while combining the species-based momentum and energy equations to obtain phase-based equations.

The sections that follow provide fundamental considerations and notation for the averaging to be done, develop appropriate forms of the averaging theorems, and apply the theorems and notation to conservation and balance equations for phases, interfaces, and common curves. Although the next section, which discusses the notation used to identify macroscale quantities, may seem a bit mundane, experience suggests that mastering the notation prior to developing and working with the larger-scale equations is wise.

6.2 Averaging Conventions and Notation

The term “averaging” is typically employed to denote normalized integration over a region. Averaging yields measures of the underlying distribution of the quantity being averaged, but these measures do not contain all of the information associated with the scale over which integration is performed. Roughly speaking, a set of smaller scale information provides a more detailed description of a system. However, the loss of information that accompanies observing a system at a larger scale is often a worthwhile trade off. For example, in transitioning the study of an ideal gas from the molecular perspective to the microscopic perspective, a tremendous loss of information about the individual molecules is inherent in using the ideal gas law rather than equations of molecular dynamics. However, the ideal gas law is of great utility in describing well a large array of gas states. What we seek in averaging microscale equations is an appropriate compression of information such that sufficient detail is retained to represent a system of interest at the larger scale with useful accuracy. This is especially important in porous medium systems because microscale details of the flow within the space between pores is not generally available. Even if one designs a porous medium composed of spherical solid grains of various sizes, calculation of the fluid dynamics within the space between the spheres for a system of more than a few million spheres is computationally overwhelming. Modeling of real porous media systems, such as groundwater aquifers or petroleum reservoirs, requires that the system behavior be described at a scale larger than the space between grains. With TCAT, this larger scale description is obtained by averaging the microscale conservation, balance, and thermodynamic equations and then closing them systematically.

When averaging porous medium systems, the integrals of microscale quantities are typically normalized by the size of the REV so that the larger scale quantities obtained are values that apply on the length scale of the REV. It is important to keep the normalization factor the same for all conservation equations so that equations of common type can be added together. For example, if the momentum for all the species is described by equations having units of momentum per averaging volume per time, these equations may be directly added together to give the momentum per volume per time for the REV as a whole.

Writing ratios of integral expressions and including those ratios in conservation equations is notationally clumsy. Explicit writing of the integrals can be avoided by defining an averaging operator that implies all the elements of the integration in shorthand form. We define the averaging operator as

$$\langle \mathcal{P}_\alpha \rangle_{\Omega_\beta,\Omega_\gamma,W} := \begin{cases} \dfrac{\int\limits_{\Omega_\beta} W\mathcal{P}_\alpha \, \mathrm{d}\mathfrak{r}}{\int\limits_{\Omega_\gamma} W \, \mathrm{d}\mathfrak{r}} & \text{for } \dim\Omega_\beta > 0,\ \dim\Omega_\gamma > 0 \\[2ex] \dfrac{\sum\limits_{\kappa\in\Omega_\beta} \mathcal{P}_{\alpha\kappa} W_\kappa}{\int\limits_{\Omega_\gamma} W \, \mathrm{d}\mathfrak{r}} & \text{for } \dim\Omega_\beta = 0,\ \dim\Omega_\gamma > 0 \\[2ex] \dfrac{\sum\limits_{\kappa\in\Omega_\beta} \mathcal{P}_{\alpha\kappa} W_\kappa}{\sum\limits_{\kappa\in\Omega_\gamma} W_\kappa} & \text{for } \dim\Omega_\beta = 0,\ \dim\Omega_\gamma = 0 \end{cases}, \tag{6.1}$$

where $\mathcal{P}_\alpha$ is a microscale property of entity α to be averaged, W is a weighting function, Ω_β is a domain of integration of the function and Ω_γ is the region of integration used in normalizing the averaging process. If W is not specified, it is assumed to be 1. Note that for cases when $\dim\Omega_\beta = 0$ or $\dim\Omega_\gamma = 0$, the "integration" is actually a summation over a set of common points and both the function being averaged and the weighting function are evaluated at the common points, κ.

Of course, a microscale function may only be integrated over a domain in which it exists. Thus, it may be surprising to see a property of entity α being averaged over the domain β. This situation exists because of the properties of a porous medium system. For example, consider a porous medium consisting of a fluid phase, w, a solid phase, s, and the interface between these phases, denoted as ws. A microscale property of the w phase, f_w, averaged over the volume occupied by the w phase within an averaging volume without a weighting function and normalized with respect to the volume occupied would be denoted $\langle f_w \rangle_{\Omega_w,\Omega_w}$. A calculation of $\langle f_w \rangle_{\Omega_s,\Omega_w}$ is meaningless since f_w does not exist in the s phase. However, in some instances, it may be desirable to average the value of f_w over the boundary of the w phase, Γ_w, normalized relative to that integration region. This would provide an average value of f_w on the boundary of Ω_w. Such an average would be denoted $\langle f_w \rangle_{\Gamma_w,\Gamma_w}$. We note that Γ_w has the same extent as Ω_{ws}, the domain of the interface. Thus, it may be convenient to replace $\langle f_w \rangle_{\Gamma_w,\Gamma_w}$ with $\langle f_w \rangle_{\Omega_{ws},\Omega_{ws}}$. When such notation is employed, it is important to remember that this latter expression actually implies an average of f_w over the boundary of the w phase that is in contact with the ws interface. The interface itself may have values of f_{ws} that are different from

f_w evaluated at the interface. The change in notation from a more precise indication of averaging over a boundary to averaging over an adjacent surface entity must be undertaken particularly carefully in instances when concentrated forces act on the surface, as discussed with regard to the solid phase stress tensor in Sect. 4.6.3.

The definition of the averaging operator in Eq. (6.1) is generally useful, but still can be notationally awkward. Therefore, three principal special cases of averaging that arise routinely are designated with further abbreviated, but less explicit, notation. These averages are referred to as the intrinsic average, the mass average, and uniquely defined averages.

6.2.1 Intrinsic Averages

The general intrinsic average is the case when $\Omega_\beta = \Omega_\gamma$ and $W = 1$ in Eq. (6.1). A general intrinsic average is denoted by adding an unadorned superscript, referring to the region of integration, to the microscale quantity being averaged such that

$$f_\alpha^\beta = \langle f_\alpha \rangle_{\Omega_\beta, \Omega_\beta} . \tag{6.2}$$

For the special case where, additionally, $\alpha = \beta$, the subscript on the intrinsic average is dropped to obtain

$$f^\alpha = \langle f_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha} . \tag{6.3}$$

We emphasize that the presence of a superscript indicates an upscaled quantity. The compressed notation for the general and special phase averages conveys a precise meaning for a macroscale variable in terms of a microscale precursor, thereby providing a desirable connection between quantities at different length scales.

6.2.2 Mass Averages

The mass average, or mass density weighted average, is obtained when the mass density of the entity associated with the quantity being averaged is the weighting function, W, in Eq. (6.1) and $\beta = \gamma$. The general mass average is indicated as

$$f_\alpha^{\overline{\beta}} = \langle f_\alpha \rangle_{\Omega_\beta, \Omega_\beta, \rho_\alpha} , \tag{6.4}$$

where the superscript with an overline denotes a mass average. As with the intrinsic average, when α is additionally equal to β, the subscript is deleted in the general mass average such that

$$f^{\overline{\alpha}} = \langle f_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha, \rho_\alpha} . \tag{6.5}$$

Properties of species are also sometimes calculated by weighting with the mass density of that species. The notation employed, analogous to that introduced in Eqs.

(6.4) and (6.5), is

$$f_{i\alpha}^{\overline{\beta}} = \langle f_{i\alpha} \rangle_{\Omega_\beta, \Omega_\beta, \rho_\alpha \omega_{i\alpha}} \tag{6.6}$$

and

$$f^{\overline{i\alpha}} = \langle f_{i\alpha} \rangle_{\Omega_\alpha, \Omega_\alpha, \rho_\alpha \omega_{i\alpha}} \ . \tag{6.7}$$

Properties of a species in an entity may also be weighted by the mass density of the entity resulting in the specific average given by

$$f^{i\overline{\alpha}} = \langle f_{i\alpha} \rangle_{\Omega_\alpha, \Omega_\alpha, \rho_\alpha} \ . \tag{6.8}$$

Note that the overbar on $f^{i\overline{\alpha}}$ extends only over the entity qualifier and not the species qualifier.

6.2.3 Unique Averages

A uniquely defined average is, as the name implies, some defined quantity expressed in terms of an average of microscale quantities, perhaps in combination with some macroscale quantities. Frequently, uniquely defined averages occur as the sum of averaged quantities. Uniquely defined averages are indicated by a superscript with a double overbar, such as $f^{\overline{\overline{\alpha}}}$, where the superscript typically refers to the domain of an entity or of a species-entity pair. The uniquely defined averages can only be related to their precursors by providing the definition in terms of the explicit averaging operator. The double overbar serves as a flag that indicates a unique definition for the upscaled variable is being used, with this definition stated in the text. The kind of averaging that has occurred is different for different properties that make use of the unique averaging shorthand.

6.2.4 Examples of Averaging Notation

It is helpful to consider some specific examples of the use of the averaging notation that will arise as the averaged conservation equations are developed. Recall that in applying the averaging operator, we will be considering the properties of the phase, interface, and common curve entities associated with an averaging volume that occupies domain Ω. The domains of various entities are denoted with a subscript on Ω.

A specific entity measure (i.e., specific volume, area, or common curve length) is defined as

$$\varepsilon^{\overline{\overline{\alpha}}} = \langle 1 \rangle_{\Omega_\alpha, \Omega} \ , \tag{6.9}$$

where $\varepsilon^{\overline{\overline{\alpha}}}$ is a volume fraction when $\alpha \in \mathfrak{I}_{\mathrm{P}}$, a specific interfacial area when $\alpha \in \mathfrak{I}_{\mathrm{I}}$, and a specific common curve length when $\alpha \in \mathfrak{I}_{\mathrm{C}}$, where the index sets of phases, interfaces, and common curves are denoted by $\mathfrak{I}_\mathrm{P}$, $\mathfrak{I}_\mathrm{I}$, and $\mathfrak{I}_\mathrm{C}$, respectively. For porous media, when one phase is a solid, the porosity is defined as

$$\varepsilon = \sum_{\alpha \in \mathfrak{I}_\mathrm{f}} \varepsilon^{\overline{\overline{\alpha}}} = 1 - \varepsilon^{\overline{\overline{s}}} , \tag{6.10}$$

where $\mathfrak{I}_\mathrm{f}$ is the index set of fluid phases. The volume fraction of a phase may equivalently be defined by making use of the indicator function as

$$\varepsilon^{\overline{\overline{\alpha}}} = \langle \Upsilon_\alpha \rangle_{\Omega,\Omega} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} , \tag{6.11}$$

where Υ_α equals 1 in the α phase and zero in all other phases.

Note that while the sum of volume fractions of all phases equals 1,

$$\sum_{\alpha \in \mathfrak{I}_\mathrm{P}} \varepsilon^{\overline{\overline{\alpha}}} = 1 , \tag{6.12}$$

a similar condition does not apply for interfaces and common curves. Specific interfacial areas and specific common curve lengths sum to the total specific interfacial area for all interfaces and total common curve length for all common curves, respectively, which is not bounded.

A fluid saturation is defined as the fraction of the non-solid portion of the averaging volume domain occupied by that fluid. This is written as

$$s^{\overline{\overline{\alpha}}} = \langle 1 \rangle_{\Omega_\alpha,\Omega_\mathrm{f}} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{f} , \tag{6.13}$$

where $\Omega_\mathrm{f} = \cup_{\alpha \in \mathfrak{I}_\mathrm{f}} \Omega_\alpha$ is the domain of the fluid phases. An equivalent definition is

$$s^{\overline{\overline{\alpha}}} = \langle \Upsilon_\alpha \rangle_{\Omega,\Omega,(1-\Upsilon_s)} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{f} . \tag{6.14}$$

The macroscale mass density is defined as an intrinsic average of the form

$$\rho^\alpha = \langle \rho_\alpha \rangle_{\Omega_\alpha,\Omega_\alpha} \quad \text{for } \alpha \in \mathfrak{I} . \tag{6.15}$$

When $\alpha \in \mathfrak{I}_\mathrm{P}$, ρ^α is the mass per volume of the phase; when $\alpha \in \mathfrak{I}_\mathrm{I}$, ρ^α is the mass per area of the interface; when $\alpha \in \mathfrak{I}_\mathrm{C}$, ρ^α is the mass per length of the common curve. Thus, the dimensions of ρ^α, and other quantities as well, change depending upon the entity qualifier.

Next, consider the macroscale velocity, which is most commonly expressed as a mass-averaged quantity of the form

$$\mathbf{v}^{\overline{\alpha}} = \langle \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega_\alpha,\rho_\alpha} \quad \text{for } \alpha \in \mathfrak{I} , \tag{6.16}$$

where the overbar indicates the weighting function is $W = \rho_\alpha$. In some cases, it is desired to obtain the mass averaged velocity of an entity at the boundary where the entity is in contact with a particular different phase. For instance, the mass average of the velocity of an α phase over the portion of the boundary of that phase in contact with an $\alpha\beta$ interface that is the boundary between the α and β phases might be written formally as

$$\mathbf{v}_{\alpha}^{\overline{\overline{\alpha\beta}}} = \langle \mathbf{v}_{\alpha} \rangle_{\Gamma_{\alpha},\Gamma_{\alpha},\rho_{\alpha}\Upsilon_{\alpha\beta}} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}}, \alpha\beta \in \mathfrak{I}_{\mathrm{I}} \,. \tag{6.17}$$

The single overbar notation of a mass average velocity cannot be employed here because integration is over the boundary of the α phase, restricted to contributions from the portion of the surface adjacent to the β phase. We can make use of the mass average notation, however, if we designate the domain of integration as $\Omega_{\alpha\beta}$. This gives

$$\mathbf{v}_{\alpha}^{\overline{\alpha\beta}} = \langle \mathbf{v}_{\alpha} \rangle_{\Omega_{\alpha\beta},\Omega_{\alpha\beta},\rho_{\alpha}} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}}, \alpha\beta \in \mathfrak{I}_{\mathrm{I}} \,. \tag{6.18}$$

The quantities on the left sides sides of Eqs. (6.17) and (6.18) are equal. However, with the notation in the latter equation, one does not have to refer back to a unique definition; this velocity is expressed as a mass average.

Other averages arise that are not readily expressible as mass or intrinsic averages. Some of these averages can be manipulated so that they can be expressed in terms of these more convenient forms. For example, consider a bulk mass density given by $\langle \rho_{\alpha} \rangle_{\Omega_{\alpha},\Omega}$, which is not an intrinsic average. A rearrangement of the domains of integration gives

$$\langle \rho_{\alpha} \rangle_{\Omega_{\alpha},\Omega} = \langle 1 \rangle_{\Omega_{\alpha},\Omega} \langle \rho_{\alpha} \rangle_{\Omega_{\alpha},\Omega_{\alpha}} = \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \,. \tag{6.19}$$

The advantage of expressing the bulk density as the product $\varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha}$ is that both of these quantities have already been defined; therefore, it is not necessary to define a new variable. In general, when averaging we seek to define the fewest number of macroscale variables, to define macroscale variables in terms of microscale precursors, and to employ variables that are experimentally accessible.

Similar to the notion used to express the bulk density, the average of the product of density and velocity can be expressed in terms of simpler variables by changing the integration domains. Thus,

$$\langle \rho_{\alpha} \mathbf{v}_{\alpha} \rangle_{\Omega_{\alpha},\Omega} = \langle 1 \rangle_{\Omega_{\alpha},\Omega} \langle \rho_{\alpha} \rangle_{\Omega_{\alpha},\Omega_{\alpha}} \langle \mathbf{v}_{\alpha} \rangle_{\Omega_{\alpha},\Omega_{\alpha},\rho_{\alpha}} = \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \mathbf{v}^{\overline{\alpha}} \,, \tag{6.20}$$

where again it can be noted that the product is expressed in terms of previously defined macroscale variables. If we are interested in the mass-weighted average of the species velocity, the weighting function is the mass of that species per entity, $\rho_{\alpha}\omega_{i\alpha}$. Then the average can be decomposed exactly to give

$$\langle \rho_{\alpha} \omega_{i\alpha} \mathbf{v}_{i\alpha} \rangle_{\Omega_{\alpha},\Omega} = \langle 1 \rangle_{\Omega_{\alpha},\Omega} \langle \rho_{\alpha} \rangle_{\Omega_{\alpha},\Omega_{\alpha}} \langle \omega_{i\alpha} \rangle_{\Omega_{\alpha},\Omega_{\alpha},\rho_{\alpha}} \langle \mathbf{v}_{\alpha} \rangle_{\Omega_{\alpha},\Omega_{\alpha},\omega_{i\alpha}\rho_{\alpha}} \,. \tag{6.21}$$

With the averages on the right expressed using the notation that has been introduced, we obtain

$$\langle \rho_{\alpha} \omega_{i\alpha} \mathbf{v}_{i\alpha} \rangle_{\Omega_{\alpha},\Omega} = \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \,. \tag{6.22}$$

Note that the mass density weighted mass fraction has an overbar only over the entity designation α because it is the mass density of that entity that provides the weighting function rather than the mass density of species in the α entity, $\rho_\alpha\omega_{i\alpha}$. We will express averages of products in terms of products of averages routinely, always being careful to seek exact expressions when possible.

Finally, consider a slightly more complicated example involving the stress tensor and a dyadic product of velocities. This quantity will be seen to arise when averaging the momentum equation. The term of interest is

$$\langle \mathbf{t}_\alpha - \rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} = \left\langle \mathbf{t}_\alpha - \rho_\alpha \left[\mathbf{v}^{\overline{\alpha}} + \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right] \left[\mathbf{v}^{\overline{\alpha}} + \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right)\right] \right\rangle_{\Omega_\alpha,\Omega} . \tag{6.23}$$

The average on the left side of Eq. (6.23) poses a problem, because the average of the dyadic product of velocities cannot be expressed completely in terms of previously defined average quantities. Because of this, the terms in brackets on the right are used as expansions of the microscale velocity by adding and subtracting macroscale velocities. The equality is exact. Since a macroscale quantity is an average over the domain, it is a constant within an averaging operator. A consequence of this is

$$\left\langle \rho_\alpha \mathbf{v}^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}} \right\rangle_{\Omega_\alpha,\Omega} = \langle \rho_\alpha \rangle_{\Omega_\alpha,\Omega} \mathbf{v}^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}} = \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{v}^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}} . \tag{6.24}$$

Also, based on Eq. (6.20), we note

$$\left\langle \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right) \mathbf{v}^{\overline{\alpha}} \right\rangle_{\Omega_\alpha,\Omega} = \langle \rho_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} \mathbf{v}^{\overline{\alpha}} - \langle \rho_\alpha \rangle_{\Omega_\alpha,\Omega} \mathbf{v}^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}} = \mathbf{0} . \tag{6.25}$$

Combination of the identities in Eqs. (6.24) and (6.25) with Eq. (6.23) yields

$$\langle \mathbf{t}_\alpha - \rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} = \left\langle \mathbf{t}_\alpha - \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right) \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right) \right\rangle_{\Omega_\alpha,\Omega} - \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{v}^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}} . \tag{6.26}$$

This equation can conveniently be written as

$$\langle \mathbf{t}_\alpha - \rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} = \varepsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{v}^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}} , \tag{6.27}$$

where

$$\mathbf{t}^{\overline{\overline{\alpha}}} = \left\langle \mathbf{t}_\alpha - \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right) \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right) \right\rangle_{\Omega_\alpha,\Omega_\alpha} . \tag{6.28}$$

Thus, the average of a sum of a microscale stress tensor plus a term involving a dyadic product of microscale velocities has been manipulated so that it can be expressed in terms of a uniquely defined macroscale stress tensor plus a dyadic product involving macroscale velocities. The dyadic velocity fluctuation product is included in the definition of the larger scale stress tensor because this contribution to stress mirrors the definition that evolves from smaller scale theories, such as kinetic theory. In other words, the subscale velocity fluctuations, not observable at the macroscale, essentially contribute to the stress tensor that is observed at the macroscale. This is a clear example of the use of a defined double-barred quantity. It will be seen subsequently that a closure relation is needed for this macroscale stress tensor, as it was for the microscale tensor, in terms of macroscale variables. Product breaking and term grouping of this nature will occur routinely in the development of the full set of conservation and balance equations that we desire. By keeping this example in mind, it will not be necessary to completely detail all the decompositions employed as the procedures used are essentially identical to those shown in this last example.

6.3 Averaging Theorems

As can be seen from Fig. 6.1, the averaging theorems are the primary workhorse for changing microscale equations to macroscale equations. Averaging theorems are applied to terms in conservation, balance, and thermodynamic equations. In the last section, a notational convention for averages was presented, and an example of product breaking was used to show how larger scale quantities can be defined in terms of smaller scale ones. The contribution of the averaging theorems is that they allow for an exchange of the order of averaging and differentiation so that the average of a derivative becomes the derivative of an average plus some ancillary terms.

The averaging theorems are tools employed in TCAT analysis and are not in themselves important products of the analysis. Put another way, the theorems facilitate the analysis, but these theorems can be used without understanding the details of the derivation. Readers wishing to understand how these non-standard theorems are derived can consult Appendix B.

The general averaging theorems are derived in Appendix B. The forms presented there apply to volumes, surfaces, curves, and points within an averaging volume. The resultant theorems are mathematical relations that apply without physical consideration of a system under study. Because we are interested in multiphase porous medium systems, it is useful to translate the notation used in the theorems to a more specific form with physical implications. For example, averaging over a volume is actually averaging over a particular phase; the boundary of a phase is an interface between phases. It will be helpful if the theorem notation reflects these facts for our applications. Additionally, we can upscale the equations using the general averaging operator that has been introduced. Later, when applying the restated theorems to a particular conservation equation, we will also be able to write some of the general averaged terms as intrinsic, mass weighted, or unique averages. For the moment, we will concentrate simply on relating the general geometric aspects of the theorems to the particular geometry of porous media.

As a prelude, we note that the naming convention for the theorems employed here is $<letter>[m,(3,0),0]$ where $<letter>$ is either D, G, or T depending on whether the theorem involves the divergence, the gradient, or the time derivative. The letter "m" takes on integer values from 0 to 3 depending on the dimensionality of the operator and the microscale region (e.g., 1 for a common curve, 3 for a volume). The number "3" in the second position indicates that the resultant operator and average are macroscopically three-dimensional. The first “0” indicates that none of the macroscopic spatial dimensions is modeled by considering fluxes across the boundary of the averaging volume (as opposed to derivative forms within the averaging volume), and the final “0” indicates that no megascale averaging is being done. In some cases, beyond the scope of what is being considered here, it is useful to perform megascale averaging over one or more dimensions. Appropriate theorems for those cases are available [5] and have been recently applied to porous media problems [4, 7].

6.3.1 Averaging Theorems for Phases

The three averaging theorems for phases are based on the theorems for volumes, Eqs. (B.12), (B.13), and (B.17) for the spatial divergence operator, gradient operator, and partial time derivative, respectively. Introduction of averaging notation is superficially straightforward but is based on some subtle points that will be emphasized in dealing with the divergence operator theorem, D[3,(3,0),0], in detail.

Theorem D[3,(3,0),0] is given by Eq. (B.12) as

$$\int\limits_{\Omega_v} \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega_v}\mathbf{f}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{v\mathrm{i}}}\mathbf{n}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,, \tag{6.29}$$

where $\mathbf{f}$ is a vector function of interest, Ω_v is the portion of the total averaging domain, Ω, over which integration is being performed, $\Gamma_{v\mathrm{i}}$ is the portion of the boundary of Ω_v that separates it from the rest of the space within Ω, and $\mathbf{n}$ is a unit normal vector on Γ_v that is outwardly directed from Ω_v. We emphasize that $\Gamma_{v\mathrm{i}}$ is not a closed boundary as it does not include the external boundary of the full averaging volume that is part of the full boundary of Ω_v.

For application to a porous medium, the region of integration is the region occupied by a phase $\alpha \in \mathfrak{J}_{\mathrm{P}}$, denoted Ω_α with a boundary within the full averaging region denoted $\Gamma_{\alpha\mathrm{i}}$. The function $\mathbf{f}$ and the unit normal, $\mathbf{n}$, are microscale properties of the α phase, and will be designated by a subscript. Thus, Eq. (6.29) for application to a porous medium system is written

$$\int\limits_{\Omega_\alpha} \nabla\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega_\alpha}\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{\alpha\mathrm{i}}}\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{P}}\,. \tag{6.30}$$

We will normalize this relation with respect to the full volume of the averaging region. Because this volume is specified to be constant, in contrast to the volumes of the phases within Ω which vary with time and position, this volume can be moved inside the divergence operator. Thus, the explicit equation we obtain is

$$\frac{\int\limits_{\Omega_\alpha} \nabla\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}} = \nabla\cdot\left(\frac{\int\limits_{\Omega_\alpha} \mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}}\right) + \frac{\int\limits_{\Gamma_{\alpha\mathrm{i}}} \mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}} \,. \tag{6.31}$$

This equation can be readily expressed using the averaging operator notation of Eq. (6.1) as

$$\langle\nabla\cdot\mathbf{f}_\alpha\rangle_{\Omega_\alpha,\Omega} = \nabla\cdot\langle\mathbf{f}_\alpha\rangle_{\Omega_\alpha,\Omega} + \langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\rangle_{\Gamma_{\alpha\mathrm{i}},\Omega} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,. \tag{6.32}$$

An additional change can be made to this expression after noting that $\Gamma_{\alpha\mathrm{i}}$ has the same mathematical coordinates as the interface domain that separates the α phase from adjacent phases. Therefore the last term in Eq. (6.32) can conveniently be expressed as an integral over the interface domains at the boundary of the phase, with one caveat. As was discussed in Sect. 4.6.3, it is possible that a concentrated force may act at the surface of a phase, particularly on a solid surface. In general, such a force could act at any point on the surface. This force is accounted for in the form of Eq. (6.32). However, if we subdivide Γ_α and consider portions of it separately, concentrated forces that act on the edges of the portions would be overlooked. For porous media, the location of a concentrated force on the solid surface will be at a common curve. When such a force acts, it is not possible to express the integral over $\Gamma_{\alpha\mathrm{i}}$ as a sum of integrals over just the interface domains because the concentrated force acts at the boundary between these domains. Thus, this singularity must be handled separately so that we write

$$\langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\rangle_{\Gamma_\alpha,\Omega} = \sum_{\kappa\in\mathfrak{I}^-_{\mathrm{c}\alpha}} \langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\rangle_{\Omega_\kappa,\Omega} + \frac{1}{2}\sum_{\beta\in\mathfrak{I}^-_{\mathrm{c}\alpha}}\ \sum_{\kappa\in\mathfrak{I}^-_{\mathrm{c}\beta}} \langle\mathbf{n}_\alpha\cdot\mathbf{f}^*_\alpha\rangle_{\Omega_\kappa,\Omega} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,. \tag{6.33}$$

In the single summation term in this equation, $\mathfrak{I}^-_{\mathrm{c}\alpha}$ is the index set of interfaces that comprise the connected set of phase α. This is the set of entities that form the boundary of entity α. For example, if we consider a system composed of three phases, *w*, *n*, and *s*, the connected set $\mathfrak{I}^-_{\mathrm{c}w}$ is the interfaces *ws* and *wn*. In the double sum term, the connected sets of interfaces to α have the index β. The connected set to these interfaces consists of both phases and common curves. Thus, the second summation is over the connected set to the β interfaces that are of dimensionality less than that of the interface denoted as the set $\mathfrak{I}^-_{\mathrm{c}\beta}$. Therefore, κ is the index of a common curve. The factor of 1/2 arises because the common curve is a connected set to both interfaces, so the double sum will encounter this common curve twice. For the three phase *w*-*n*-*s* system, κ corresponds to the locus of the *wns* common curve. The common curves in contact with the α phase must be accounted for if a concentrated force acts at that location. This force is designated using a superscript *. In the absence of any concentrated force, the term involving the double sum is zero, and the integral over $\Gamma_{\alpha\mathrm{i}}$ is equivalent to the integral over the domain of the interface entities that separate Ω_α from adjacent phases. We emphasize that the

Table 6.1 Convenient forms of the averaging theorems for porous media analysis based on general forms derived in Appendix B

Entity	Name	Averaging Theorem	Eq.
Phase $\alpha \in \mathfrak{J}_{\mathrm{P}}$	D[3,(3,0),0]	$\langle \nabla \cdot \mathbf{f}_\alpha \rangle_{\Omega_\alpha,\Omega} = \nabla \cdot \langle \mathbf{f}_\alpha \rangle_{\Omega_\alpha,\Omega} + \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha \cdot \mathbf{f}_\alpha \rangle_{\Omega_\kappa,\Omega} + \frac{1}{2} \sum\limits_{\beta \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\beta}^-} \langle \mathbf{n}_\alpha \cdot \mathbf{f}_\alpha^* \rangle_{\Omega_\kappa,\Omega}$	(B.12)
	G[3,(3,0),0]	$\langle \nabla f_\alpha \rangle_{\Omega_\alpha,\Omega} = \nabla \langle f_\alpha \rangle_{\Omega_\alpha,\Omega} + \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha f_\alpha \rangle_{\Omega_\kappa,\Omega} + \frac{1}{2} \sum\limits_{\beta \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\beta}^-} \langle \mathbf{n}_\alpha f_\alpha^* \rangle_{\Omega_\kappa,\Omega}$	(B.13)
	T[3,(3,0),0]	$\left\langle \frac{\partial f_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \frac{\partial}{\partial t} \langle f_\alpha \rangle_{\Omega_\alpha,\Omega} - \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\kappa f_\alpha \rangle_{\Omega_\kappa,\Omega} - \frac{1}{2} \sum\limits_{\beta \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\beta}^-} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\kappa f_\alpha^* \rangle_{\Omega_\kappa,\Omega}$	(B.17)
Interface $\alpha \in \mathfrak{J}_{\mathrm{I}}$	D[2,(3,0),0]	$\langle \nabla' \cdot \mathbf{f}_\alpha \rangle_{\Omega_\alpha,\Omega} = \nabla \cdot \left\langle \mathsf{l}'_\alpha \cdot \mathbf{f}_\alpha \right\rangle_{\Omega_\alpha,\Omega} - \left\langle \nabla' \cdot \mathsf{l}'_\alpha \cdot \mathbf{f}_\alpha \right\rangle_{\Omega_\alpha,\Omega} + \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha \cdot \mathbf{f}_\alpha \rangle_{\Omega_\kappa,\Omega}$	(B.36)
	G[2,(3,0),0]	$\langle \nabla' f_\alpha \rangle_{\Omega_\alpha,\Omega} = \nabla \cdot \left\langle \mathsf{l}'_\alpha f_\alpha \right\rangle_{\Omega_\alpha,\Omega} - \left\langle \nabla' \cdot \mathsf{l}'_\alpha f_\alpha \right\rangle_{\Omega_\alpha,\Omega} + \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha f_\alpha \rangle_{\Omega_\kappa,\Omega}$	(B.37)
	T[2,(3,0),0]	$\left\langle \frac{\partial' f_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \frac{\partial}{\partial t} \langle f_\alpha \rangle_{\Omega_\alpha,\Omega} + \nabla \cdot \left\langle \left(\mathsf{I} - \mathsf{l}'_\alpha \right) \cdot \mathbf{v}_\alpha f_\alpha \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \nabla' \cdot \mathsf{l}'_\alpha \cdot \mathbf{v}_\alpha f_\alpha \right\rangle_{\Omega_\alpha,\Omega} - \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\kappa f_\alpha \rangle_{\Omega_\kappa,\Omega}$	(B.46)
Curve $\alpha \in \mathfrak{J}_{\mathrm{C}}$	D[1,(3,0),0]	$\langle \nabla'' \cdot \mathbf{f}_\alpha \rangle_{\Omega_\alpha,\Omega} = \nabla \cdot \langle \mathbf{l}_\alpha \mathbf{l}_\alpha \cdot \mathbf{f}_\alpha \rangle_{\Omega_\alpha,\Omega} - \langle \mathbf{l}_\alpha \cdot \nabla'' \mathbf{l}_\alpha \cdot \mathbf{f}_\alpha \rangle_{\Omega_\alpha,\Omega} + \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha \cdot \mathbf{f}_\alpha \rangle_{\Omega_\kappa,\Omega}$	(B.66)
	G[1,(3,0),0]	$\langle \nabla'' f_\alpha \rangle_{\Omega_\alpha,\Omega} = \nabla \cdot \langle \mathbf{l}_\alpha \mathbf{l}_\alpha f_\alpha \rangle_{\Omega_\alpha,\Omega} - \langle \mathbf{l}_\alpha \cdot \nabla'' \mathbf{l}_\alpha f_\alpha \rangle_{\Omega_\alpha,\Omega} + \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha f_\alpha \rangle_{\Omega_\kappa,\Omega}$	(B.67)
	T[1,(3,0),0]	$\left\langle \frac{\partial'' f_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \frac{\partial}{\partial t} \langle f_\alpha \rangle_{\Omega_\alpha,\Omega} + \nabla \cdot \langle (\mathsf{I} - \mathbf{l}_\alpha \mathbf{l}_\alpha) \cdot \mathbf{v}_\alpha f_\alpha \rangle_{\Omega_\alpha,\Omega} + \langle \mathbf{l}_\alpha \cdot \nabla'' \mathbf{l}_\alpha \cdot \mathbf{v}_\alpha f_\alpha \rangle_{\Omega_\alpha,\Omega} - \sum\limits_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^-} \langle \mathbf{n}_\alpha \cdot \mathbf{v}_\kappa f_\alpha \rangle_{\Omega_\kappa,\Omega}$	(B.71)
Point $\alpha \in \mathfrak{J}_{\mathrm{Pt}}$	T[0,(3,0),0]	$\left\langle \frac{\partial''' f_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \frac{\partial}{\partial t} \langle f_\alpha \rangle_{\Omega_\alpha,\Omega} + \nabla \cdot \langle \mathbf{v}_\alpha f_\alpha \rangle_{\Omega_\alpha,\Omega}$	(B.73)

decomposition suggested by Eq. (6.33) does not formally indicate integration of the property of an α phase over a surface entity, which has its own properties. However, because of the geometry that exists for a porous medium system, this notational decomposition is convenient.

Equation (6.33) can be substituted into Eq. (6.32) to obtain the divergence averaging theorem D[3,(3,0),0] provided as the first entry in Table 6.1. No additional notational conventions are needed to obtain G[3,(3,0),0] from the general form, Eq. (B.13) in Appendix B. For theorem T[3,(3,0),0], one additional convention is required. Note that the last term of Eq. (B.17) involves the velocity of that boundary in the direction normal to the boundary, $\mathbf{n}\cdot\mathbf{w}$. For the α phase, we can denote this as $\mathbf{n}_\alpha\cdot\mathbf{w}_\alpha$. In the $\mathbf{n}_\alpha$ direction, the velocity of the boundary is equal to the velocity of the material in the boundary. Thus, we replace $\mathbf{n}_\alpha\cdot\mathbf{w}_\alpha$ by $\mathbf{n}_\alpha\cdot\mathbf{v}_\kappa$ where $\kappa \in \mathfrak{I}^-_{c\alpha}$ and break the boundary into parts, depending on the interface present, when writing T[3,(3,0),0]. Caution is advised, however. Although the normal components of the velocity of $\Gamma_{\alpha\mathrm{i}}$ and of Ω_κ for $\kappa \in \mathfrak{I}^-_{c\alpha}$ must be the same, the tangential components need not be the same. The velocity of the boundary in the tangential direction can be different from the velocity of the material moving within the boundary in the same way that the average velocity of fluid flowing between two plates can be different from the velocity of the plates in the tangential direction but must be equal to the velocity of the plates in the normal direction[2].

6.3.2 Averaging Theorems for Interfaces

It is useful to also explore briefly the notational conventions that are used with the averaging theorems for interfaces. We will begin with the general form of D[2,(3,0),0] given as Eq. (B.36),

$$\int_{\Omega_s} \nabla'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int_{\Omega_s} \mathbf{l}'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int_{\Omega_s} \nabla'\cdot\mathbf{l}'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \int_{\Gamma_{s\mathrm{i}}} \mathbf{n}'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,, \tag{6.34}$$

where $\mathbf{f}$ is a vector function of interest that is a property of the interface entity in the two-dimensional domain Ω_s that is within the averaging volume Ω; $\Gamma_{s\mathrm{i}}$ is the portion of the boundary of Ω_s that separates it from other interfaces within Ω; $\mathbf{n}'$ is a unit vector normal to $\Gamma_{s\mathrm{i}}$ and tangent to Ω_s; $\mathbf{l}$ is the unit tensor; and $\mathbf{l}'$ is the unit tensor minus the dyad of the normal to the surface and thus is a tensor in the surface. Note that $\mathbf{f}$ is a three-dimensional vector that may have components tangent and normal to the interface. This equation may be adapted to the microscale notation so that the surface is identified with the index α where $\alpha \in \mathfrak{I}_\mathrm{I}$. Thus Eq. (6.34) may be rewritten as

$$\int_{\Omega_\alpha} \nabla'\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int_{\Omega_\alpha} \mathbf{l}'_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} - \int_{\Omega_\alpha} \nabla'\cdot\mathbf{l}'_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} + \int_{\Gamma_{\alpha\mathrm{i}}} \mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I}\,. \tag{6.35}$$

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[2] The distinction between the velocity of a domain and the velocity of material within the domain has been a source of confusion and error in modeling porous medium systems [3, 6].

Although the domain of integration is an interface, we will normalize Eq. (6.35) with respect to the total volume of the averaging region. The normalized equation is

$$\frac{\int\limits_{\Omega_\alpha} \nabla'\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}} = \nabla\cdot\left(\frac{\int\limits_{\Omega_\alpha}\mathbf{l}'_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}}\right) - \frac{\int\limits_{\Omega_\alpha}\nabla'\cdot\mathbf{l}'_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega}\mathrm{d}\mathfrak{r}} + \frac{\int\limits_{\Gamma_{\alpha\mathrm{i}}}\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega}\mathrm{d}\mathfrak{r}}\,, \tag{6.36}$$

which may be written using the notational convention of Eq. (6.1) as

$$\left\langle\nabla'\cdot\mathbf{f}_\alpha\right\rangle_{\Omega_\alpha,\Omega} = \nabla\cdot\left\langle\mathbf{l}'_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Omega_\alpha,\Omega} - \left\langle\nabla'\cdot\mathbf{l}'_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Omega_\alpha,\Omega} + \left\langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Gamma_{\alpha\mathrm{i}},\Omega} \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{I}}\,. \tag{6.37}$$

In this equation, the last term represents an integral over the boundary of the interface which is coincident with a common curve.

For the case of a two-phase porous media system, no boundaries of surfaces exist within the system. For a three-phase system, there will be at most one common curve type. When the system is composed of four or more phases, the boundary of the surface will be coincident with common curve segments and common points that lie on the boundary. At the locations of these common points, concentrated forces can occur. Thus the boundary may be decomposed to portions represented as the domain of the bounding common curve with

$$\left\langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Gamma_\alpha,\Omega} = \sum_{\kappa\in\mathfrak{J}^-_{\mathrm{c}\alpha}}\left\langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Omega_\kappa,\Omega} + \frac{1}{2}\sum_{\beta\in\mathfrak{J}^-_{\mathrm{c}\alpha}}\;\sum_{\kappa\in\mathfrak{J}^-_{\mathrm{c}\beta}}\left\langle\mathbf{n}_\alpha\cdot\mathbf{f}^*_\alpha\right\rangle_{\Omega_\kappa,\Omega} \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{I}}\,. \tag{6.38}$$

In this equation $\mathfrak{J}^-_{\mathrm{c}\alpha}$ is the index set of entities connected to the interface with dimension less than that of the interface (i.e. a dimension of 1), which includes the common curves at the edge of interface α. The double sum accounts for common points along the boundary curve where concentrated, singular forces act.

The D[2,(3,0),0] theorem is obtained by substitution of Eq. (6.38) into Eq. (6.37). The result is provided in Table 6.1 with the common point terms omitted since these will not be considered in subsequent analysis. Thus the term involving integration over the boundary of the interface is represented simply as an integral over the common curve domains that are coincident with this boundary. Theorems G[2,(3,0),0] and T[2,(3,0),0] are also provided in the table. They are obtained by making notational changes to their general forms, Eqs. (B.37) and (B.46), following the same considerations as provided here explicitly for D[2,(3,0),0] and noting that the normal velocity of the boundary of the surface is equal to the velocity of the material in the common curve κ, where $\kappa\in\mathfrak{J}^-_{\mathrm{c}\alpha}$.

6.3.3 Averaging Theorems for Common Curves

For the common curve, the general divergence theorem is D[1,(3,0),0], given in Eq. (B.66) as

$$\int\limits_{\Omega_c} \nabla''\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega_c} \mathbf{l}\mathbf{l}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_c} \mathbf{l}\cdot\nabla''\mathbf{l}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \sum_{\kappa\in\Gamma_{\mathrm{ci}}} \mathbf{n}''\cdot\mathbf{f}\,|_{\kappa}\ , \tag{6.39}$$

where **f** is a three-dimensional vector function of interest that is a property of the common curve entity in the one-dimensional domain, Ω_c, that is within the averaging volume, Ω; Γ_{ci} is the boundary domain of the common curve consisting of the points at the end of the curve segments; $\mathbf{n}''$ is a unit vector tangent to the common curve and outwardly directed at the end points of the common curve domain; and **l** is a unit vector tangent to the common curve. Adaptation of this equation to the microscale notation with the curve identified by the index α gives

$$\int\limits_{\Omega_\alpha} \nabla''\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega_\alpha} \mathbf{l}_\alpha\mathbf{l}_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha} \mathbf{l}_\alpha\cdot\nabla''\mathbf{l}_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r} + \sum_{\kappa\in\Gamma_{\alpha\mathrm{i}}} \mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\,|_{\kappa} \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{C}}\ . \tag{6.40}$$

Normalization of this equation by the averaging domain then provides

$$\frac{\int\limits_{\Omega_\alpha} \nabla''\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}} = \nabla\cdot\left(\frac{\int\limits_{\Omega_\alpha} \mathbf{l}_\alpha\mathbf{l}_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}}\right) + \frac{\int\limits_{\Omega_\alpha} \mathbf{l}_\alpha\cdot\nabla''\mathbf{l}_\alpha\cdot\mathbf{f}_\alpha\,\mathrm{d}\mathfrak{r}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}} + \frac{\sum\limits_{\kappa\in\Gamma_{\alpha\mathrm{i}}} \mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\,|_{\kappa}}{\int\limits_{\Omega} \mathrm{d}\mathfrak{r}}\ . \tag{6.41}$$

Introduction of the notation convention of Eq. (6.1) yields

$$\left\langle\nabla''\cdot\mathbf{f}_\alpha\right\rangle_{\Omega_\alpha,\Omega} = \nabla\cdot\left\langle\mathbf{l}_\alpha\mathbf{l}_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Omega_\alpha,\Omega} + \left\langle\mathbf{l}_\alpha\cdot\nabla''\mathbf{l}_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Omega_\alpha,\Omega} + \left\langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Gamma_{\alpha\mathrm{i}},\Omega} \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{C}}\ . \tag{6.42}$$

The boundary term in this expression can be handled quite readily. The boundary of the common curve is a collection of points that are coincident with common points. Thus, the average over the boundary of the common curve is a summation such that

$$\left\langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Gamma_{\alpha\mathrm{i}},\Omega} = \sum_{\kappa\in\mathfrak{I}^{-}_{\mathrm{c}\alpha}} \left\langle\mathbf{n}_\alpha\cdot\mathbf{f}_\alpha\right\rangle_{\Omega_\kappa,\Omega}\ . \tag{6.43}$$

Because the boundary of the common curve is a discrete set of points, there is no need to be concerned about singular functions that occur at locations where the boundary is discretized into subdomains, as with the boundary of a phase or interface. Thus insertion of Eq. (6.43) into Eq. (6.42) provides the entry for D[1,(3,0),0] that appears in Table 6.1. Theorems G[1,(3,0),0] and T[1,(3,0),0] are also provided in the table based on Eqs. (B.67) and (B.71) with appropriate modification of notation, including the fact that the velocity of the common point on the boundary is equal to the velocity of material associated with the common point.

6.3.4 Averaging Theorem for Common Points

Neither the D[0,(3,0),0] nor the G[0,(3,0),0] averaging theorems exist for a common point because the microscale spatial derivative of a function that exists only at a point is undefined. Theorem T[0,(3,0),0] given in Eq. (B.73) is

$$\sum_{\kappa\in\Omega_{pt}} \left.\frac{\partial''' f}{\partial t}\right|_{\kappa} = \frac{\partial}{\partial t}\left(\sum_{\kappa\in\Omega_{pt}} f|_{\kappa}\right) + \nabla\cdot\left(\sum_{\kappa\in\Omega_{pt}} (\mathbf{v}f)|_{\kappa}\right) . \tag{6.44}$$

Because the common points have no boundaries, there is no need to give special consideration to any boundary terms. Additionally, the notation convention of Eq. (6.1) applies to sums over points as well as integration over regions. Statement of the averaging theorem in the simplified notation is accomplished easily by explicitly noting that the microscale properties apply to a function in Ω_α for $\alpha \in \mathfrak{I}_{\mathrm{Pt}}$. Normalization with respect to the averaging volume provides the last row in Table 6.1.

6.4 Application of Averaging Process

With the averaging theorems in hand, Fig. 6.1 indicates that the next desired step is to transform the microscale equations to macroscale forms. The microscale equations have been developed in Chap. 2. Entity- and species-based microscale equations for phases and interfaces appear in Sects. 2.3 and 2.4, respectively. In these sections, tables are given where the equations are collected. The microscale equations for phases are transformed to the macroscale using the [3,(3,0),0] family of averaging theorems, while the equations for an interface make use of the [2,(3,0),0] family. The equations for a common curve are similar in essence to those for an interface. Thus, rather than being formally derived, they are inferred from the interface forms and are given in Sect. 2.5. These equations are converted to the macroscale using theorems in the [1,(3,0),0] family. The common point conservation equations may similarly be derived based on the general microscale form given in section 2.6 using equation T[0,(3,0),0]. As will be seen, the similarities in form of all macroscale equations for a particular property also suggest direct inference of macroscale common point conservation equations.

Implementation of the averaging process is straightforward. It consists of applying the averaging operator, $\langle\cdot\rangle_{\Omega_\alpha,\Omega}$, to a microscale conservation equation, making use of the averaging theorems to exchange the order of differentiation and averaging, and then breaking the products so that all quantities are expressed in terms of phase averages, mass-weighted averages, or unique averages. Averaging is applied to the partial derivative forms of the microscale equations. For example, the average of general equation Eq. (2.120) gives

$$\begin{aligned}\langle \mathcal{F}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} =& \left\langle \frac{\partial^{(n)} F_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \nabla^{(n)} \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) \right\rangle_{\Omega_\alpha,\Omega} - \langle S_{\Omega T i\alpha} \rangle_{\Omega_\alpha,\Omega} \\ & - \left\langle \mathrm{div}^{(n)} \left(\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}_\alpha^{(n)} \right) \right\rangle_{\Omega_\alpha,\Omega} - \langle G_{\Omega i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0 \\ & \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}, n = 3 - \dim \alpha \, . \end{aligned} \quad (6.45)$$

The T averaging theorem from the [dim α, (3, 0), 0] family will be applied to the time derivative, and the D theorem from this family will be applied to the two terms involving the divergence operator.[3] After application of the averaging theorems, the resultant expressions can be evaluated using the averaging operator. What is not obvious is the selection of the definitions of macroscale quantities such that they will not vary from one equation to the next. For example, the mass density of a phase should be the same macroscale quantity in the mass, momentum, energy, entropy, and gravitational potential equations. This definition will be seen to fall out easily. Definitions that are more complex and not obvious involve the stress tensor, the non-advective energy flux, and other terms. Thus we will derive the equations paying particular attention to the definitions of the variables.

6.5 Macroscale Principles for a Phase

The goal of this section is to develop the sets of macroscale conservation and balance equations for a species in a phase and for the material comprising the phase as a whole. The definitions and notational conventions developed in Sect. 6.2 will be used. The derivation of equations will proceed from conservation of mass to momentum, energy, entropy, and the gravitational potential with emphasis on the definitions employed for unique averages. The macroscale phase equations developed in this section are the larger-scale conservation and entropy equations in Fig. 6.1.

6.5.1 Conservation of Mass

The microscale conservation of mass equation for a species in a phase may be found in Table 2.1 and is given also as Eq. (2.17). Application of the averaging operator to this equation yields

$$\langle \mathcal{M}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = \left\langle \frac{\partial(\rho_\alpha \omega_{i\alpha})}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \langle \nabla \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}) \rangle_{\Omega_\alpha,\Omega} - \langle r_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0$$

---

[3] Recall that the $\nabla^{(n)} \cdot$ operator contracts the first index of the quantity it operates on, the index of $\mathbf{v}_{i\alpha}$, while the $\mathrm{div}^{(n)}$ operator contracts the last index of the quantity it operates on, the second index of $\mathbf{l}_\alpha^{(n)}$.

$$\text{for } \alpha \in \mathfrak{I}_{\mathrm{P}} \,. \tag{6.46}$$

Application of T[3,(3,0),0] and G[3,(3,0),0] from Table 6.1 to the first and second terms, respectively, exchanges the order of averaging and differentiation such that

$$\begin{aligned}\langle \mathcal{M}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = {} & \frac{\partial}{\partial t} \langle \rho_\alpha \omega_{i\alpha} \rangle_{\Omega_\alpha,\Omega} + \nabla\cdot \langle \rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} - \langle r_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \\ & - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\alpha}} \langle \rho_\alpha \omega_{i\alpha} \left(\mathbf{v}_\kappa - \mathbf{v}_{i\alpha} \right) \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} = 0 \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}} \,. \end{aligned} \tag{6.47}$$

The double summation in the averaging theorems accounting for concentrated forces, or singularities, is dropped in the mass balance equation because no such processes for flow are considered to occur here. The connected set of entities given by $\mathfrak{I}_{\mathrm{c}\alpha}$ includes all the interfaces that separate the α phase from adjacent phases.

With the macroscale mass density, ρ^α, defined by Eq. (6.15), the mass-averaged mass fraction and velocity, $\omega^{i\overline{\alpha}}$ and $\mathbf{v}^{\overline{i\alpha}}$, defined by Eq. (6.22), and the volume fraction of α defined according to Eq. (6.9), Eq. (6.47) may be rewritten as

$$\begin{aligned}\mathcal{M}^{\overline{\overline{i\alpha}}} := \frac{\partial \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \right)}{\partial t} + \nabla\cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) - \varepsilon^{\overline{\overline{\alpha}}} r^{i\alpha} - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\alpha}} \overset{i\kappa\to i\alpha}{M} = 0 \\ \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}} \,, \end{aligned} \tag{6.48}$$

where $r^{i\alpha}$ is the intrinsic average production rate of species i. The equation designation $\mathcal{M}^{\overline{\overline{i\alpha}}}$ satisfies the definition

$$\mathcal{M}^{\overline{\overline{i\alpha}}} := \langle \mathcal{M}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \,. \tag{6.49}$$

It refers specifically to the statement of terms as indicated on the right side of Eq. (6.48) but not to any rearrangement of these terms that also would satisfy Eq. (6.49). We emphasize that the defining statement of Eq. (6.49) confirms that $\mathcal{M}^{\overline{\overline{i\alpha}}}$ is an averages species mass conservation equation; Eq. (6.48) defines the specific form of the macroscale species conservation that $\mathcal{M}^{\overline{\overline{i\alpha}}}$ connotes. We also have denoted the mass exchange of species i between the α and κ entities when $\kappa \in \mathfrak{I}_{\mathrm{c}\alpha}$ as

$$\overset{i\kappa\to i\alpha}{M} = \begin{cases} -\langle \rho_\alpha \omega_{i\alpha} \left(\mathbf{v}_{i\alpha} - \mathbf{v}_\kappa \right) \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} & \text{if } \kappa \in \mathfrak{I}_{\mathrm{c}\alpha}^{-} \\ \langle \rho_\kappa \omega_{i\kappa} \left(\mathbf{v}_{i\kappa} - \mathbf{v}_\alpha \right) \cdot \mathbf{n}_\kappa \rangle_{\Omega_\alpha,\Omega} & \text{if } \kappa \in \mathfrak{I}_{\mathrm{c}\alpha}^{+} \end{cases} \,. \tag{6.50}$$

When $\alpha \in \mathfrak{I}_{\mathrm{P}}$, as is the present case, only the first of these options is encountered. However, in anticipation of subsequent work with interfaces and common curves that can exchange mass with entities of both higher and lower dimensionality, we provide the general definition in Eq. (6.50).

It is very important to recognize that the mass density, mass fraction, and unit normal in Eq. (6.50) are all the properties of the higher-dimensional entity participating in the exchange. Thus, a simple exchange of the α and κ indices, regardless of which refers to a phase and which to an interface, provides

$$\overset{i\kappa\to i\alpha}{M} = -\overset{i\alpha\to i\kappa}{M} \tag{6.51}$$

since the mass exchange from a κ entity to an α entity is the negative of the exchange from the α entity to a κ entity. This means that the following definition holds:

$$\overset{i\alpha\to i\kappa}{M} = -\langle \rho_\alpha \omega_{i\alpha} (\mathbf{v}_\kappa - \mathbf{v}_{i\alpha}) \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^- \,. \tag{6.52}$$

However, in contrast to what one might be tempted to write by a simple exchange of the α and κ indices in this equation,

$$\overset{i\kappa\to i\alpha}{M} \neq -\langle \rho_\kappa \omega_{i\kappa} (\mathbf{v}_\alpha - \mathbf{v}_{i\kappa}) \cdot \mathbf{n}_\kappa \rangle_{\Omega_\alpha,\Omega} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^- \,. \tag{6.53}$$

In working with exchange terms, the properties in the averaging operator are always those of the higher dimension entity (with the exception of the velocity of the boundary), and the integration is over the lower-dimensional entity.

Equation (6.48) can be written in material derivative form, after applying the product rule to the second term and then regrouping, as

$$\mathcal{M}_*^{\overline{\overline{i\alpha}}} := \frac{\mathrm{D}^{\overline{i\alpha}}\left(\epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\right)}{\mathrm{D}t} + \epsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{i\alpha}}} - \epsilon^{\overline{\overline{\alpha}}} r^{i\alpha} - \sum_{\kappa\in\mathcal{J}_{c\alpha}} \overset{i\kappa\to i\alpha}{M} = 0$$

$$\text{for } \alpha \in \mathcal{J}_\mathrm{P} \,, \tag{6.54}$$

where the material derivative with respect to the mass-averaged species velocity is

$$\frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t} = \frac{\partial}{\partial t} + \mathbf{v}^{\overline{i\alpha}} \cdot \nabla \,, \tag{6.55}$$

the macroscale rate of strain tensor is defined as

$$\mathbf{d}^{\overline{\overline{i\alpha}}} = \frac{1}{2}\left[\nabla \mathbf{v}^{\overline{i\alpha}} + \left(\nabla \mathbf{v}^{\overline{i\alpha}}\right)^\mathrm{T}\right] \,, \tag{6.56}$$

and

$$\mathsf{I}{:}\mathbf{d}^{\overline{\overline{i\alpha}}} = \nabla \cdot \mathbf{v}^{\overline{i\alpha}} \,. \tag{6.57}$$

Observe that $\mathbf{d}^{\overline{\overline{i\alpha}}}$ is defined using double overbar notation because it is not simply an average of its microscale precursor but instead is defined in terms of a mass averaged velocity. The designation $\mathcal{M}_*^{\overline{\overline{i\alpha}}}$ refers specifically to the species mass conservation form given in Eq. (6.54). Although $\mathcal{M}^{\overline{\overline{i\alpha}}} = \mathcal{M}_*^{\overline{\overline{i\alpha}}} = 0$, it is useful to retain the notion that each refers to a species mass conservation equation written in a particular way. For convenience, the forms of species conservation given as $\mathcal{M}^{\overline{\overline{i\alpha}}}$ and $\mathcal{M}_*^{\overline{\overline{i\alpha}}}$ in Eqs. (6.48) and (6.54), respectively, are readily accessible from Table 6.2.

Table 6.2 Physical variables for species-based macroscale equations in partial derivative or material form. $\mathcal{M}^{i\alpha}$, $\boldsymbol{\mathcal{P}}^{i\alpha}$, $\mathcal{E}^{i\alpha}$, $\mathcal{S}^{i\alpha}$, and $\mathcal{G}^{i\alpha}$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential for species i in entity α. In the last term, $(n) = 3 - \dim\alpha$, is the number of primes that appear where $\dim\alpha$ is the dimensionality of the α entity. Singularity terms in $S_{\Omega}^{\overline{\overline{i\alpha}}}$ are denoted with an asterisk

$$\begin{aligned}\mathcal{F}^{\overline{\overline{i\alpha}}} := {} & \frac{\partial F^{\overline{\overline{i\alpha}}}}{\partial t} + \nabla\cdot\left(\mathbf{v}^{\overline{i\alpha}} F^{\overline{\overline{i\alpha}}}\right) - S_{\Omega}^{\overline{\overline{i\alpha}}} - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}} \sum_{j\in\mathfrak{J}_s} \overset{j\kappa\to i\alpha}{X} - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{+}}\sum_{j\in\mathfrak{J}_s}\overset{j\kappa\to i\alpha}{X^{*}} \\ & -\mathrm{div}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{S}_{\Gamma}^{\overline{\overline{i\alpha}}}\right) - \frac{1}{2} \sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}} \left\langle \mathbf{S}^{*}_{\Gamma_{i\alpha}}\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\kappa,\Omega} - G_{\Omega}^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } i\in\mathfrak{J}_s, \alpha\in\mathfrak{J}\end{aligned}$$

$$\begin{aligned}\mathcal{F}_{*}^{\overline{\overline{i\alpha}}} := {} & \frac{\mathrm{D}^{\overline{i\alpha}} F^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} + F^{\overline{\overline{i\alpha}}}\mathsf{I}{:}\mathbf{d}^{\overline{i\alpha}} - S_{\Omega}^{\overline{\overline{i\alpha}}} - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}} \sum_{j\in\mathfrak{J}_s} \overset{j\kappa\to i\alpha}{X} - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{+}}\sum_{j\in\mathfrak{J}_s}\overset{j\kappa\to i\alpha}{X^{*}} \\ & -\mathrm{div}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{S}_{\Gamma}^{\overline{\overline{i\alpha}}}\right) - \frac{1}{2} \sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}} \left\langle \mathbf{S}^{*}_{\Gamma_{i\alpha}}\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\kappa,\Omega} - G_{\Omega}^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } i\in\mathfrak{J}_s, \alpha\in\mathfrak{J}\end{aligned}$$

$\mathcal{F}^{i\alpha}$	$F^{\overline{\overline{i\alpha}}}$	$S_{\Omega}^{\overline{\overline{i\alpha}}}$	$\overset{j\kappa\to i\alpha}{X}$	$\mathbf{S}_{\Gamma}^{\overline{\overline{i\alpha}}}$	$G_{\Omega}^{\overline{\overline{i\alpha}}}$
$\mathcal{M}^{i\alpha}$	$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}$	—	$\delta_{ij}\overset{i\kappa\to i\alpha}{M}$	—	$\varepsilon^{\overline{\overline{\alpha}}}r^{i\alpha}$
$\boldsymbol{\mathcal{P}}^{i\alpha}$	$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}$	$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}$	$\delta_{ij}\overset{i\kappa\to i\alpha}{M}\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}} + \overset{j\kappa\to i\alpha}{\mathbf{T}}$	$\mathbf{t}^{\overline{\overline{i\alpha}}}$	$\varepsilon^{\overline{\overline{\alpha}}}\left(\mathbf{p}^{\overline{\overline{i\alpha}}} + r^{i\alpha}\mathbf{v}^{\overline{i\alpha}}\right)$
$\mathcal{E}^{i\alpha}$	$E^{\overline{\overline{i\alpha}}}$ $+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\dfrac{\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}}{2}$ $+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}K_E^{\overline{\overline{i\alpha}}}$	$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}$ $+\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{i\alpha}}}$ $+\varepsilon^{\overline{\overline{\alpha}}}h^{i\alpha}$	$\delta_{ij}\overset{i\kappa\to i\alpha}{M}\left(\overline{E}_i^{\overline{\overline{\alpha,\kappa}}} + \dfrac{\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}}{2} + K_{Ei}^{\overline{\overline{\alpha,\kappa}}}\right) + \overset{j\kappa\to i\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{i\alpha,j\kappa}}} + \overset{j\kappa\to i\alpha}{Q}$	$\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\cdot\mathbf{v}^{\overline{i\alpha}}$ $+\mathbf{q}^{\overline{\overline{i\alpha}}}$	$\varepsilon^{\overline{\overline{\alpha}}}\left(e^{\overline{\overline{i\alpha}}} + \mathbf{p}^{\overline{\overline{i\alpha}}}\cdot\mathbf{v}^{\overline{i\alpha}} + r^{i\alpha}\dfrac{\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}}{2} + r^{i\alpha}K_E^{\overline{\overline{i\alpha}}}\right)$
$\mathcal{S}^{i\alpha} - \Lambda^{\overline{\overline{i\alpha}}}$	$\eta^{\overline{\overline{i\alpha}}}$	$\varepsilon^{\overline{\overline{\alpha}}}b^{i\alpha}$	$\delta_{ij}\overset{i\kappa\to i\alpha}{M}\overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}} + \overset{j\kappa\to i\alpha}{\Phi}$	$\boldsymbol{\varphi}^{\overline{\overline{i\alpha}}}$	$\Lambda^{\overline{\overline{i\alpha}}}$
$\mathcal{G}^{i\alpha}$	$\Psi^{\overline{\overline{i\alpha}}}$	$-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}$ $-\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{i\alpha}}}$	$\delta_{ij}\overset{i\kappa\to i\alpha}{M}\psi_i^{\overline{\overline{\alpha,\kappa}}} + \overset{i\kappa\to i\alpha}{G}$	$\mathbf{q}_{\mathbf{g}}^{\overline{\overline{i\alpha}}}$	$\left\langle\rho_\alpha\omega_{i\alpha}\left[\dfrac{\partial^{(n)}\psi_{i\alpha}}{\partial t} + \mathbf{v}_{i\alpha}\cdot\left(\mathsf{I} - \mathsf{I}_{\alpha}^{(n)}\right)\cdot\mathbf{g}_{i\alpha}\right]\right\rangle_{\Omega_\alpha,\Omega} + \langle r_{i\alpha}\psi_{i\alpha}\rangle_{\Omega_\alpha,\Omega}$

Inter-entity Exchange Terms

$$\overset{i\kappa\to i\alpha}{M} = \left\langle\underset{i\kappa\to i\alpha}{M}\right\rangle_{\Omega_\alpha,\Omega} \quad \text{for } \dim\kappa > \dim\alpha$$

$$\overset{i\kappa\to i\alpha}{M} = \left\langle\underset{i\kappa\to i\alpha}{M}\right\rangle_{\Omega_\kappa,\Omega} \quad \text{for } \dim\kappa < \dim\alpha$$

$$\overset{j\kappa\to i\alpha}{\mathbf{T}} = \left\langle\underset{j\kappa\to i\alpha}{\mathbf{T}} + \delta_{ij}\underset{i\kappa\to i\alpha}{M}\left(\mathbf{v}_{i\kappa} - \mathbf{v}_{i\kappa}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} \quad \text{for } \dim\kappa > \dim\alpha$$

$$\overset{j\kappa\to i\alpha}{\mathbf{T}} = \left\langle\underset{j\kappa\to i\alpha}{\mathbf{T}} + \delta_{ij}\underset{i\kappa\to i\alpha}{M}\left(\mathbf{v}_{i\alpha} - \mathbf{v}_{i\alpha}^{\overline{\kappa}}\right)\right\rangle_{\Omega_\kappa,\Omega} \quad \text{for } \dim\kappa < \dim\alpha$$

$$\overset{j\kappa\to i\alpha}{Q} = \left\langle\underset{j\kappa\to i\alpha}{Q} + \underset{j\kappa\to i\alpha}{\mathbf{T}}\cdot\left(\mathbf{v}_{j\kappa} - \mathbf{v}_{j\kappa}^{\overline{\alpha}}\right) + \delta_{ij}\underset{i\kappa\to i\alpha}{M}\left[\overline{E}_{i\kappa} + K_{Ei\alpha\kappa} - \left(\overline{E}_{i\kappa}^{\overline{\alpha}} + K_{Ei\kappa}^{\overline{\overline{\alpha}}}\right)\right]\right\rangle_{\Omega_\alpha,\Omega} \quad \text{for } \dim\kappa > \dim\alpha$$

$$\overset{j\kappa\to i\alpha}{Q} = \left\langle\underset{j\kappa\to i\alpha}{Q} + \underset{j\kappa\to i\alpha}{\mathbf{T}}\cdot\left(\mathbf{v}_{i\alpha} - \mathbf{v}_{i\alpha}^{\overline{\kappa}}\right) + \delta_{ij}\underset{i\kappa\to i\alpha}{M}\left[\overline{E}_{i\alpha} + K_{Ei\alpha\kappa} - \left(\overline{E}_{i\alpha}^{\overline{\kappa}} + K_{Ei\alpha}^{\overline{\overline{\kappa}}}\right)\right]\right\rangle_{\Omega_\kappa,\Omega} \quad \text{for } \dim\kappa < \dim\alpha$$

$$\overset{j\kappa\to i\alpha}{\Phi} = \left\langle\underset{j\kappa\to i\alpha}{\Phi} + \delta_{ij}\underset{i\kappa\to i\alpha}{M}\left(\overline{\eta}_{i\kappa} - \overline{\eta}_{i\kappa}^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} \quad \text{for } \dim\kappa > \dim\alpha$$

$$\overset{j\kappa\to i\alpha}{\Phi} = \left\langle\underset{j\kappa\to i\alpha}{\Phi} + \delta_{ij}\underset{i\kappa\to i\alpha}{M}\left(\overline{\eta}_{i\alpha} - \overline{\eta}_{i\alpha}^{\overline{\kappa}}\right)\right\rangle_{\Omega_\kappa,\Omega} \quad \text{for } \dim\kappa < \dim\alpha$$

For the α phase as a whole, we begin with Eq. (2.21), which is also available from Table 2.2. Introduction of the averaging operator to this equation gives

$$\langle \mathcal{M}_\alpha \rangle_{\Omega_\alpha,\Omega} = \left\langle \frac{\partial \rho_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \langle \nabla\cdot(\rho_\alpha \mathbf{v}_\alpha)\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,. \tag{6.58}$$

Application of averaging theorems T[3,(3,0),0] and D[3,(3,0),0] yields

$$\begin{aligned}\langle \mathcal{M}_\alpha \rangle_{\Omega_\alpha,\Omega} =& \frac{\partial}{\partial t}\langle \rho_\alpha \rangle_{\Omega_\alpha,\Omega} + \nabla\cdot\langle \rho_\alpha \mathbf{v}_\alpha \rangle_{\Omega_\alpha,\Omega} \\ &- \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \langle \rho_\alpha (\mathbf{v}_\kappa - \mathbf{v}_\alpha)\cdot\mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} = 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,. \end{aligned} \tag{6.59}$$

Making use of the notation for the various averages, we simplify the statement of this equation to

$$\mathcal{M}^{\overline{\overline{\alpha}}} := \frac{\partial\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\right)}{\partial t} + \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha \mathbf{v}^{\overline{\alpha}}\right) - \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{M} = 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,, \tag{6.60}$$

where the mass exchange from the κ interface to the α phase satisfies the first line of the more general definition

$$\overset{\kappa\to\alpha}{M} = \sum_{i\in\mathfrak{I}_s} \overset{i\kappa\to i\alpha}{M} = \begin{cases} \langle \rho_\alpha (\mathbf{v}_\kappa - \mathbf{v}_\alpha)\cdot\mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} & \text{if } \kappa \in \mathfrak{I}^-_{\mathrm{c}\alpha} \\ \langle \rho_\kappa (\mathbf{v}_\kappa - \mathbf{v}_\alpha)\cdot\mathbf{n}_\kappa \rangle_{\Omega_\alpha,\Omega} & \text{if } \kappa \in \mathfrak{I}^+_{\mathrm{c}\alpha} \end{cases} . \tag{6.61}$$

After rearrangement to material derivative form, Eq. (6.60) becomes

$$\mathcal{M}_*^{\overline{\overline{\alpha}}} := \frac{\mathrm{D}^{\overline{\alpha}}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\right)}{\mathrm{D}t} + \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha \mathsf{I}{:}\mathsf{d}^{\overline{\overline{\alpha}}} - \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{M} = 0 \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,, \tag{6.62}$$

where the material derivative with respect to the mass-averaged phase velocity is

$$\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t} = \frac{\partial}{\partial t} + \mathbf{v}^{\overline{\alpha}}\cdot\nabla \,. \tag{6.63}$$

and the rate of strain tensor is defined as

$$\mathsf{d}^{\overline{\overline{\alpha}}} = \frac{1}{2}\left[\nabla\mathbf{v}^{\overline{\alpha}} + \left(\nabla\mathbf{v}^{\overline{\alpha}}\right)^{\mathrm{T}}\right] \,. \tag{6.64}$$

The distinction between the forms of the equations denoted by the notation $\mathcal{M}^{\overline{\overline{\alpha}}}$ vs. $\mathcal{M}_*^{\overline{\overline{\alpha}}}$ is important to recognize. Equations (6.60) and (6.62) are collected in Table 6.3.

Summation of Eq. (6.48) over all species in phase α should provide an expression for the mass conservation equation equivalent to Eq. (6.60). Thus, we calculate,

Table 6.3 Physical variables for entity-based macroscale equations in partial derivative or material form. $\mathcal{M}^{\overline{\overline{\alpha}}}$, $\boldsymbol{\mathcal{P}}^{\overline{\overline{\alpha}}}$, $\mathcal{E}^{\overline{\overline{\alpha}}}$, $\mathcal{S}^{\overline{\overline{\alpha}}}$, and $\mathcal{G}^{\overline{\overline{\alpha}}}$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential for entity α. In the last term, $(n) = 3 - \dim\alpha$ is the number of primes that appear, where $\dim\alpha$ is the dimensionality of the α entity. Singularity terms denoted in $S_{\Omega}^{\overline{\overline{\alpha}}}$ with an asterisk are set to zero unless $\dim\alpha = 3$

$$\mathcal{F}^{\overline{\overline{\alpha}}} := \frac{\partial F^{\overline{\overline{\alpha}}}}{\partial t} + \nabla\cdot\left(\mathbf{v}^{\overline{\alpha}} F^{\overline{\overline{\alpha}}}\right) - S_{\Omega}^{\overline{\overline{\alpha}}} - \sum_{\kappa\in\mathfrak{I}_{c\alpha}} \overset{\kappa\to\alpha}{X} - \frac{1}{2} \sum_{\beta\in\mathfrak{I}^{+}_{c\alpha}} \sum_{\kappa\in\mathfrak{I}^{+}_{c\beta}} \overset{\kappa\to\alpha}{X^{*}}$$
$$-\operatorname{div}\left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{S}_{\Gamma}^{\overline{\overline{\alpha}}}\right) - \frac{1}{2} \sum_{\beta\in\mathfrak{I}^{-}_{c\alpha}} \sum_{\kappa\in\mathfrak{I}^{-}_{c\beta}} \left\langle \mathbf{S}^{*}_{\Gamma\alpha} \cdot \mathbf{n}_{\alpha} \right\rangle_{\Omega_\kappa,\Omega} - G_{\Omega}^{\overline{\overline{\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{I}$$

$$\mathcal{F}_{*}^{\overline{\overline{\alpha}}} := \frac{\mathrm{D}^{\overline{\alpha}} F^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + F^{\overline{\overline{\alpha}}} \mathsf{I}{:}\mathbf{d}^{\overline{\alpha}} - S_{\Omega}^{\overline{\overline{\alpha}}} - \sum_{\kappa\in\mathfrak{I}_{c\alpha}} \overset{\kappa\to\alpha}{X} - \frac{1}{2} \sum_{\beta\in\mathfrak{I}^{+}_{c\alpha}} \sum_{\kappa\in\mathfrak{I}^{+}_{c\beta}} \overset{\kappa\to\alpha}{X^{*}}$$
$$-\operatorname{div}\left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{S}_{\Gamma}^{\overline{\overline{\alpha}}}\right) - \frac{1}{2} \sum_{\beta\in\mathfrak{I}^{-}_{c\alpha}} \sum_{\kappa\in\mathfrak{I}^{-}_{c\beta}} \left\langle \mathbf{S}^{*}_{\Gamma\alpha} \cdot \mathbf{n}_{\alpha} \right\rangle_{\Omega_\kappa,\Omega} - G_{\Omega}^{\overline{\overline{\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{I}$$

$\mathcal{F}^{\alpha}$	$F^{\overline{\overline{\alpha}}}$	$S_{\Omega}^{\overline{\overline{\alpha}}}$	$\overset{\kappa\to\alpha}{X}$	$\mathbf{S}_{\Gamma}^{\overline{\overline{\alpha}}}$	$G_{\Omega}^{\overline{\overline{\alpha}}}$
$\mathcal{M}^{\alpha}$	$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}$	—	$\overset{\kappa\to\alpha}{M}$	—	—
$\boldsymbol{\mathcal{P}}^{\alpha}$	$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}$	$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}$	$\overset{\kappa\to\alpha}{M}\,\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} + \overset{\kappa\to\alpha}{\mathbf{T}}$	$\mathbf{t}^{\overline{\overline{\alpha}}}$	—
$\mathcal{E}^{\alpha}$	$E^{\overline{\overline{\alpha}}}$ $+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\dfrac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}$ $+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}K_{E}^{\overline{\overline{\alpha}}}$	$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}$ $+\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}$ $+\varepsilon^{\overline{\overline{\alpha}}}h^{\alpha}$	$\overset{\kappa\to\alpha}{M}\Big(\overline{E}^{\overline{\overline{\alpha,\kappa}}}$ $+\dfrac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}}{2} + K_{E}^{\overline{\overline{\alpha,\kappa}}}\Big)$ $+\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} + \overset{\kappa\to\alpha}{Q}$	$\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}$ $+\mathbf{q}^{\overline{\overline{\alpha}}}$	—
$\mathcal{S}^{\alpha} - \Lambda^{\overline{\overline{\alpha}}}$	$\eta^{\overline{\overline{\alpha}}}$	$\varepsilon^{\overline{\overline{\alpha}}}b^{\alpha}$	$\overset{\kappa\to\alpha}{M}\,\overline{\eta}^{\overline{\overline{\alpha,\kappa}}} + \overset{\kappa\to\alpha}{\Phi}$	$\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}$	$\Lambda^{\overline{\overline{\alpha}}}$
$\mathcal{G}^{\alpha}$	$\Psi^{\overline{\overline{\alpha}}}$	$-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}$ $-\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}$	$\overset{i\kappa\to i\alpha}{M}\,\psi^{\overline{\overline{\alpha,\kappa}}} + \overset{\kappa\to\alpha}{G}$	$\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}$	$\displaystyle\sum_{i\in\mathfrak{I}_s}\Big\langle\rho_{\alpha}\omega_{i\alpha}\Big[\frac{\partial^{(n)}\psi_{i\alpha}}{\partial t}$ $+\mathbf{v}_{i\alpha}\cdot\left(\mathsf{I}-\mathsf{I}_{\alpha}^{(n)}\right)\cdot\mathbf{g}_{i\alpha}\Big]\Big\rangle_{\Omega_\alpha,\Omega}$ $\displaystyle+\sum_{i\in\mathfrak{I}_s}\langle r_{i\alpha}\psi_{i\alpha}\rangle_{\Omega_\alpha,\Omega}$

Inter-entity Exchange Terms
$\overset{\kappa\to\alpha}{M} = \left\langle \underset{\kappa\to\alpha}{M} \right\rangle_{\Omega_\alpha,\Omega}$ for dim $\kappa >$ dim α
$\overset{\kappa\to\alpha}{M} = \left\langle \underset{\kappa\to\alpha}{M} \right\rangle_{\Omega_\kappa,\Omega}$ for dim $\kappa <$ dim α
$\overset{\kappa\to\alpha}{\mathbf{T}} = \left\langle \underset{\kappa\to\alpha}{\mathbf{T}} + \underset{\kappa\to\alpha}{M}(\mathbf{v}_{\kappa} - \mathbf{v}_{\kappa}^{\overline{\alpha}}) \right\rangle_{\Omega_\alpha,\Omega}$ for dim $\kappa >$ dim α
$\overset{\kappa\to\alpha}{\mathbf{T}} = \left\langle \underset{\kappa\to\alpha}{\mathbf{T}} + \underset{\kappa\to\alpha}{M}(\mathbf{v}_{\alpha} - \mathbf{v}_{\alpha}^{\overline{\kappa}}) \right\rangle_{\Omega_\kappa,\Omega}$ for dim $\kappa <$ dim α
$\overset{\kappa\to\alpha}{Q} = \left\langle \underset{\kappa\to\alpha}{Q} + \underset{\kappa\to\alpha}{\mathbf{T}}\cdot(\mathbf{v}_{\kappa} - \mathbf{v}_{\kappa}^{\overline{\alpha}}) + \underset{\kappa\to\alpha}{M}\left[\overline{E}_{\kappa} + K_{E\alpha\kappa} + K_{E\kappa} - \left(\overline{E}_{\kappa}^{\overline{\alpha}} + K_{E\kappa}^{\overline{\overline{\alpha}}}\right)\right] \right\rangle_{\Omega_\alpha,\Omega}$ for dim $\kappa >$ dim α
$\overset{\kappa\to\alpha}{Q} = \left\langle \underset{\kappa\to\alpha}{Q} + \underset{\kappa\to\alpha}{\mathbf{T}}\cdot(\mathbf{v}_{\alpha} - \mathbf{v}_{\alpha}^{\overline{\kappa}}) + \underset{\kappa\to\alpha}{M}\left[\overline{E}_{\alpha} + K_{E\alpha\kappa} + K_{E\alpha} - \left(\overline{E}_{\alpha}^{\overline{\kappa}} + K_{E\alpha}^{\overline{\overline{\kappa}}}\right)\right] \right\rangle_{\Omega_\kappa,\Omega}$ for dim $\kappa <$ dim α
$\overset{\kappa\to\alpha}{\Phi} = \left\langle \underset{\kappa\to\alpha}{\Phi} + \underset{\kappa\to\alpha}{M}(\overline{\eta}_{\kappa} - \overline{\eta}_{\kappa}^{\overline{\alpha}}) \right\rangle_{\Omega_\alpha,\Omega}$ for dim $\kappa >$ dim α
$\overset{\kappa\to\alpha}{\Phi} = \left\langle \underset{\kappa\to\alpha}{\Phi} + \underset{\kappa\to\alpha}{M}(\overline{\eta}_{\alpha} - \overline{\eta}_{\alpha}^{\overline{\kappa}}) \right\rangle_{\Omega_\kappa,\Omega}$ for dim $\kappa <$ dim α

while exchanging the order of differentiation and summation,

$$\sum_{i\in\mathfrak{J}_s}\mathcal{M}^{\overline{\overline{i\alpha}}}=\frac{\partial}{\partial t}\left(\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\right)+\nabla\cdot\left(\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\right)$$
$$-\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}r^{i\alpha}-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\left(\sum_{i\in\mathfrak{J}_s}\overset{i\kappa\to i\alpha}{M}\right)=0\quad\text{for }\alpha\in\mathfrak{J}_{\mathrm{P}}\,.\tag{6.65}$$

A comparison of this equation with Eq. (6.60) shows immediately that the two equations are identical when

$$\mathcal{M}^{\overline{\overline{\alpha}}}=\sum_{i\in\mathfrak{J}_s}\mathcal{M}^{\overline{\overline{i\alpha}}}\,,\tag{6.66}$$

$$1=\sum_{i\in\mathfrak{J}_s}\omega^{i\overline{\alpha}}\,,\tag{6.67}$$

$$\mathbf{v}^{\overline{\alpha}}=\sum_{i\in\mathfrak{J}_s}\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\,,\tag{6.68}$$

$$0=\sum_{i\in\mathfrak{J}_s}r^{i\alpha}\,,\tag{6.69}$$

and

$$\overset{\kappa\to\alpha}{M}=\sum_{i\in\mathfrak{J}_s}\overset{i\kappa\to i\alpha}{M}\qquad\text{for }\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}\,.\tag{6.70}$$

Besides being mathematically necessary, these conditions are also physically reasonable.

For some applications, we will make use of the macroscale diffusion velocity defined as

$$\mathbf{u}^{\overline{\overline{i\alpha}}}=\mathbf{v}^{\overline{i\alpha}}-\mathbf{v}^{\overline{\alpha}}\,.\tag{6.71}$$

With this definition, Eqs. (6.67) and (6.68) show that when entity α is composed of N chemical species, only $N-1$ of the diffusion velocities are independent since

$$\sum_{i\in\mathfrak{J}_s}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}=\mathbf{0}\,.\tag{6.72}$$

Thus, a problem can be posed equivalently in terms of $\mathbf{v}^{\overline{\alpha}}$ along with $N-1$ diffusion velocities, $\mathbf{u}^{\overline{\overline{i\alpha}}}$, or in terms of N species velocities, $\mathbf{v}^{\overline{i\alpha}}$.

With Eq. (6.71) substituted into Eq. (6.48) we obtain

$$\frac{\partial\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\right)}{\partial t}+\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}\right)+\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right)$$
$$-\varepsilon^{\overline{\overline{\alpha}}}r^{i\alpha}-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{i\kappa\to i\alpha}{M}=0\quad\text{for }\alpha\in\mathfrak{J}_{\mathrm{P}}\,.\tag{6.73}$$

This equation may be rearranged to a material derivative form as

$$\begin{aligned}\mathcal{M}_{**}^{\overline{\overline{i\alpha}}} :=& \frac{\mathrm{D}^{\overline{\alpha}}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\right)}{\mathrm{D}t} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{\alpha}}} + \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right) \\ &- \varepsilon^{\overline{\overline{\alpha}}}r^{i\alpha} - \sum_{\kappa\in\mathcal{J}_{c\alpha}} \overset{i\kappa\to i\alpha}{M} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\mathrm{P}} ,\end{aligned} \tag{6.74}$$

where we have used the notation $\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$ to distinguish this particular form of species mass conservation from those in $\mathcal{M}^{\overline{\overline{i\alpha}}}$ and $\mathcal{M}_{*}^{\overline{\overline{i\alpha}}}$.

Clearly, several notationally different but mathematically equivalent forms of the conservation of mass equation for a species in a phase can be written. Each of the forms introduced will be of use in certain situations. However, all of the different forms are equivalent statements of the same principle. The equations derived here resemble equations that appear routinely in the literature. However, here the equations have been formulated by careful averaging from microscale precursors, which has provided macroscale variables that are all explicitly defined in terms of microscale variables. These definitions provide the bases for connections across length scales. Similar connections will be sought for all macroscale equations that we develop. These precise definitions and interscale relations are essential components of TCAT models that enable specification of experimental measurements and microscale simulation approaches to test the resultant TCAT models.

6.5.2 Conservation of Momentum

A similar approach to that detailed in deriving macroscale mass conservation equations for a phase can be used to derive conservation of momentum equations for a species in a phase and for the phase as a whole. To develop the macroscale species momentum equation, we begin with the microscale form, Eq. (2.26), which can also be constructed based on Table 2.1. Averaging of $\mathcal{P}_{i\alpha}$ over Ω_α within an averaging volume and using the domain of the volume as the normalizing region yields

$$\begin{aligned}\langle\mathcal{P}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} =& \left\langle\frac{\partial(\rho_\alpha\omega_{i\alpha}\mathbf{v}_{i\alpha})}{\partial t}\right\rangle_{\Omega_\alpha,\Omega} + \langle\nabla\cdot(\rho_\alpha\omega_{i\alpha}\mathbf{v}_{i\alpha}\mathbf{v}_{i\alpha})\rangle_{\Omega_\alpha,\Omega} - \langle\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} \\ &- \left\langle\nabla\cdot\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\right\rangle_{\Omega_\alpha,\Omega} - \langle\mathbf{p}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \langle r_{i\alpha}\mathbf{v}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} = \mathbf{0} \\ & \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_{\mathrm{P}} .\end{aligned} \tag{6.75}$$

Averaging theorem T[3,(3,0),0] is applied to the time derivative term, and D[3,(3,0),0] is applied to the two terms involving the average of the divergence so that we have

$$\langle\mathcal{P}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} = \frac{\partial}{\partial t}\langle\rho_\alpha\omega_{i\alpha}\mathbf{v}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} + \nabla\cdot\langle\rho_\alpha\omega_{i\alpha}\mathbf{v}_{i\alpha}\mathbf{v}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \langle\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\rangle_{\Omega_\alpha,\Omega}$$

$$
\begin{aligned}
&- \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \langle \rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} (\mathbf{v}_\kappa - \mathbf{v}_{i\alpha}) \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} - \nabla \cdot \left\langle \mathbf{t}_{i\alpha}{}^{\mathrm{T}} \right\rangle_{\Omega_\alpha,\Omega} \\
&- \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \langle \mathbf{t}_{i\alpha} \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} - \frac{1}{2} \sum_{\beta \in \mathfrak{I}_{c\alpha}^-} \sum_{\kappa \in \mathfrak{I}_{c\beta}^-} \langle \mathbf{t}_{i\alpha}^* \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} \\
&- \langle \mathbf{p}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} - \langle r_{i\alpha} \mathbf{v}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = \mathbf{0} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{P}} \,. \qquad (6.76)
\end{aligned}
$$

Note that since the microscale divergence of the stress tensor designates contraction with the second index on the stress by using the transpose of the tensor, the unit normal in the boundary terms also contracts the second index. Because no concentrated flow at the common curve was considered in the mass conservation equation, no concentrated momentum flux at the common curve is included here. However, a singularity of the stress tensor is allowed by the term with the double summation.

We now break the average of the product $\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}$ into a product of averages using Eq. (6.22). Also the average of $\mathbf{t}_{i\alpha}{}^{\mathrm{T}} - \rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \mathbf{v}_{i\alpha}$ can be changed to terms involving the average of products analogously to Eq. (6.27) using the species based stress tensor and velocity vectors. Applying these two procedures to Eq. (6.76), defining some unique averages, and regrouping of terms yields

$$
\begin{aligned}
\langle \mathcal{P}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = {} & \frac{\partial}{\partial t} \left(\epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) + \nabla \cdot \left(\epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) - \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{g}^{\overline{i\alpha}} \\
& - \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \langle [\mathbf{t}_{i\alpha} + \rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} (\mathbf{v}_\kappa - \mathbf{v}_{i\alpha})] \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} \\
& - \frac{1}{2} \sum_{\beta \in \mathfrak{I}_{c\alpha}^-} \sum_{\kappa \in \mathfrak{I}_{c\beta}^-} \langle \mathbf{t}_{i\alpha}^* \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} - \nabla \cdot \left(\epsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}} \right) \\
& - \epsilon^{\overline{\overline{\alpha}}} \mathbf{p}^{\overline{\overline{i\alpha}}} - \epsilon^{\overline{\overline{\alpha}}} r^{i\alpha} \mathbf{v}^{\overline{i\alpha}} = \mathbf{0} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{P}} \,, \qquad (6.77)
\end{aligned}
$$

where

$$
\mathbf{g}^{\overline{i\alpha}} = \langle \mathbf{g}_{i\alpha} \rangle_{\Omega_\alpha,\Omega_\alpha,\rho_\alpha\omega_{i\alpha}} \,, \qquad (6.78)
$$

$$
\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}} = \left\langle \mathbf{t}_{i\alpha}{}^{\mathrm{T}} - \rho_\alpha \omega_{i\alpha} \left(\mathbf{v}_{i\alpha} - \mathbf{v}^{\overline{i\alpha}} \right) \left(\mathbf{v}_{i\alpha} - \mathbf{v}^{\overline{i\alpha}} \right) \right\rangle_{\Omega_\alpha,\Omega_\alpha} \,, \qquad (6.79)
$$

and

$$
\mathbf{p}^{\overline{\overline{i\alpha}}} = \left\langle \mathbf{p}_{i\alpha} + r_{i\alpha} \left(\mathbf{v}_{i\alpha} - \mathbf{v}^{\overline{i\alpha}} \right) \right\rangle_{\Omega_\alpha,\Omega_\alpha} \,. \qquad (6.80)
$$

Finally, the summation terms that involve exchanges from the α phase to interfaces in its connected set and to the common curve can be expressed in special forms to obtain

$$
\begin{aligned}
\mathcal{P}^{\overline{\overline{i\alpha}}} := {} & \frac{\partial}{\partial t} \left(\epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) + \nabla \cdot \left(\epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) - \epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{g}^{\overline{i\alpha}} \\
& - \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \overset{i\kappa\to i\alpha}{M} \mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \sum_{j \in \mathfrak{I}_s} \overset{j\kappa\to i\alpha}{\mathbf{T}} - \frac{1}{2} \sum_{\beta \in \mathfrak{I}_{c\alpha}^-} \sum_{\kappa \in \mathfrak{I}_{c\beta}^-} \sum_{j \in \mathfrak{I}_s} \overset{j\kappa\to i\alpha}{\mathbf{T}^*}
\end{aligned}
$$

$$-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\right)-\varepsilon^{\overline{\overline{\alpha}}}\mathbf{p}^{\overline{\overline{i\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}r^{i\alpha}\mathbf{v}^{\overline{i\alpha}}=\mathbf{0}\quad\text{for } i\in\mathfrak{J}_s,\alpha\in\mathfrak{J}_{\mathrm{P}}\ , \tag{6.81}$$

where

$$\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}=\begin{cases}\mathbf{v}_{i\alpha}^{\overline{\kappa}} & \text{if } \kappa\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}\\ \mathbf{v}_{i\kappa}^{\overline{\alpha}} & \text{if } \kappa\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}\end{cases}\ . \tag{6.82}$$

For a phase, the connected set consists only of interfaces. Thus, the only option from Eq. (6.82) that is needed for use in Eq. (6.81) is $\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}=\mathbf{v}_{i\alpha}^{\overline{\kappa}}$. Interfaces and common curves interact with entities of both higher and lower dimensionality. Therefore, the options in Eq. (6.82) will both come into play subsequently when considering equations for those entities. Additionally when dim $\kappa <$dim α, as is the case here,

$$\overset{j\kappa\to i\alpha}{\mathbf{T}}=\left\langle\left[\underset{j\kappa\to i\alpha}{z_T}\mathbf{t}_{i\alpha}+\delta_{ij}\rho_\alpha\omega_{i\alpha}\left(\mathbf{v}_{i\alpha}-\mathbf{v}_{i\alpha}^{\overline{\kappa}}\right)(\mathbf{v}_\kappa-\mathbf{v}_{i\alpha})\right]\cdot\mathbf{n}_\alpha\right\rangle_{\Omega_\kappa,\Omega} \tag{6.83}$$

and

$$\sum_{j\in\mathfrak{J}_s}\underset{j\kappa\to i\alpha}{z_T}=1\ . \tag{6.84}$$

On the other hand, if dim $\kappa >$dim α, as will arise for interfaces and common curves,

$$\overset{j\kappa\to i\alpha}{\mathbf{T}}=-\left\langle\left[\underset{j\kappa\to i\alpha}{z_T}\mathbf{t}_{j\kappa}+\delta_{ij}\rho_\kappa\omega_{i\kappa}\left(\mathbf{v}_{i\kappa}-\mathbf{v}_{i\kappa}^{\overline{\alpha}}\right)(\mathbf{v}_\alpha-\mathbf{v}_{i\kappa})\right]\cdot\mathbf{n}_\kappa\right\rangle_{\Omega_\alpha,\Omega} \tag{6.85}$$

and

$$\sum_{i\in\mathfrak{J}_s}\underset{j\kappa\to i\alpha}{z_T}=1\ . \tag{6.86}$$

The conditions for $\overset{j\kappa\to i\alpha}{\mathbf{T}^*}$ are the same as for $\overset{j\kappa\to i\alpha}{\mathbf{T}}$, except the latter parts that are multiplied by δ_{ij} are excluded as they would be associated with a concentrated inter-entity mass exchange.

The summation terms in Eq. (6.81) account for momentum transfer from the connected set of interfaces to species i in the α phase. These transfers occur as a byproduct of mass transfer, due to interfacial stress, and because of any concentrated forces on the surface of the α phase that act where interfaces meet at the surface. Because stress can be transferred from all species in the interface to species i in the α phase, a summation over all species is employed for the stress term. Additionally, we observe that the inter-entity transfer terms are expressed universally in terms of variables in a higher-dimensional entity evaluated at the entity boundary, which is comprised of lower-dimensional entities. What is transferred from one entity must go into an adjacent entity for overall system conservation to be satisfied. For example, it follows that, based on Eqs. (6.51) and (6.82),

$$\overset{i\alpha\to i\kappa}{M}\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}=\overset{i\alpha\to i\kappa}{M}\mathbf{v}_{i\alpha}^{\overline{\kappa}}=-\overset{i\kappa\to i\alpha}{M}\mathbf{v}_{i\alpha}^{\overline{\kappa}}\quad\text{for }\alpha\in\mathfrak{J}_{\mathrm{P}},\kappa\in\mathfrak{J}_{\mathrm{c}\alpha} \tag{6.87}$$

and

$$\overset{j\kappa\to i\alpha}{\mathbf{T}} = -\overset{i\alpha\to j\kappa}{\mathbf{T}} \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{P}}, \kappa \in \mathfrak{J}_{\mathrm{c}\alpha} \, . \tag{6.88}$$

The introduction of the parameters z_T is arbitrary in that any set that satisfies Eq. (6.84) is allowable. However, the coefficient is used here to account for the fact that the stress on a species in the interface can be exerted by any species in the adjacent phases. The particular selection of the set of coefficients indicated here makes the subsequent combination of terms possible. The selection of these coefficients accounts for the exchange between species i in the α phase and species j in the $\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}$ interface. The macroscopic momentum conservation equation, Eq. (6.81), appears in Table 6.2. The momentum exchange terms in this table are forms that are notationally simpler but not as transparent in the identification of variables as those given in Eqs. (6.83) and (6.85). Additionally, Table 6.2 lists a momentum exchange term, the double sum of $\delta_{ij} \overset{i\kappa\to i\alpha}{M^*} \mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}} + \overset{j\kappa\to i\alpha}{\mathbf{T}^*}$, that involves entities that are two dimensions higher than the entity of interest. For a phase or interface, no such higher-dimensional entity exists, so the term is ignored. It will be shown subsequently that this term arises naturally in the analysis of common curve momentum. Similar terms involving concentrated sources also appear for the momentum, energy, and entropy equations in both Tables 6.2 and 6.3. These terms may be nonzero when the α entity is a common curve or common point, as will be discussed in some detail. Furthermore, a double sum of $\left\langle \mathbf{S}^*_{\Gamma_{i\alpha}} \cdot \mathbf{n}_\alpha \right\rangle_{\Omega_\kappa,\Omega}$ is listed that involves integration over entities two dimensions lower than the entity of interest. This term is zero for common points and common curves, but could be included in analyses of a phase or interface. For a phase, this term accounts for interaction with the common curve; while for an interface, this term would account for interactions with common points. In the absence of a concentrated non-advective flux, this term is zero.

The material derivative form of the macroscale species momentum equation is obtained by first applying the product rule to the second term in Eq. (6.81) so that

$$\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\mathbf{v}^{\overline{i\alpha}}\right) = \mathbf{v}^{\overline{i\alpha}}\cdot\nabla\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\right) + \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{i\alpha}}} \, . \tag{6.89}$$

Substitution of this relation into Eq. (6.81) and combining terms to obtain the material derivative with respect to $\mathbf{v}^{\overline{i\alpha}}$ gives

$$\begin{aligned}
\mathcal{P}_*^{\overline{\overline{i\alpha}}} := {} & \frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\right) + \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}} \\
& - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}} \overset{i\kappa\to i\alpha}{M} \mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}} \sum_{j\in\mathfrak{J}_s} \overset{j\kappa\to i\alpha}{\mathbf{T}} - \frac{1}{2} \sum_{\beta\in\mathfrak{J}^-_{\mathrm{c}\alpha}} \sum_{\kappa\in\mathfrak{J}^-_{\mathrm{c}\beta}} \sum_{j\in\mathfrak{J}_s} \overset{j\kappa\to i\alpha}{\mathbf{T}^*} \\
& - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\right) - \varepsilon^{\overline{\overline{\alpha}}}\mathbf{p}^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}r^{i\alpha}\mathbf{v}^{\overline{i\alpha}} = \mathbf{0} \quad \text{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J}_{\mathrm{P}} \, .
\end{aligned} \tag{6.90}$$

The conservation of momentum for a phase entity may be obtained by averaging Eq. (2.27) from the microscale to the macroscale or by summing Eq. (6.81) over all N species in the phase. Both approaches must, and do, provide the same result. Here, we will illustrate the summation approach to obtain

$$\begin{aligned}\sum_{i\in\mathcal{J}_s} \mathcal{P}^{\overline{\overline{i\alpha}}} = {} & \frac{\partial}{\partial t}\left(\sum_{i\in\mathcal{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\right) + \nabla\cdot\left(\sum_{i\in\mathcal{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{v}^{\overline{i\alpha}}\mathbf{v}^{\overline{i\alpha}}\right)\\ & - \sum_{i\in\mathcal{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}} - \sum_{i\in\mathcal{J}_s}\sum_{\kappa\in\mathcal{J}_{c\alpha}} \overset{i\kappa\to i\alpha}{M}\,\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}} - \sum_{i\in\mathcal{J}_s}\sum_{\kappa\in\mathcal{J}_{c\alpha}}\sum_{j\in\mathcal{J}_s} \overset{j\kappa\to i\alpha}{\mathbf{T}}\\ & - \frac{1}{2}\sum_{i\in\mathcal{J}_s}\sum_{\beta\in\mathcal{J}_{c\alpha}^{-}}\sum_{\kappa\in\mathcal{J}_{c\beta}^{-}}\sum_{j\in\mathcal{J}_s} \overset{j\kappa\to i\alpha}{\mathbf{T}^{*}} - \sum_{i\in\mathcal{J}_s}\nabla\cdot\left(\sum_{i\in\mathcal{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\right)\\ & - \sum_{i\in\mathcal{J}_s}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{p}^{\overline{\overline{i\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} r^{i\alpha}\mathbf{v}^{\overline{i\alpha}}\right) = \mathbf{0} \quad \text{for } i\in\mathcal{J}_s, \alpha\in\mathcal{J}_{\mathrm{P}}\,. \end{aligned} \tag{6.91}$$

Making use of the definitions given in Eqs. (6.67)–(6.71), we obtain

$$\begin{aligned}\mathcal{P}^{\overline{\overline{\alpha}}} := {} & \frac{\partial}{\partial t}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\right) + \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}\right) - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}} - \sum_{\kappa\in\mathcal{J}_{c\alpha}} \overset{\kappa\to\alpha}{M}\,\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\\ & - \sum_{\kappa\in\mathcal{J}_{c\alpha}} \overset{\kappa\to\alpha}{\mathbf{T}} - \frac{1}{2}\sum_{\beta\in\mathcal{J}_{c\alpha}^{-}}\sum_{\kappa\in\mathcal{J}_{c\beta}^{-}} \overset{\kappa\to\alpha}{\mathbf{T}^{*}} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right) = \mathbf{0} \quad \text{for } \alpha\in\mathcal{J}_{\mathrm{P}}\,, \end{aligned} \tag{6.92}$$

where

$$\mathcal{P}^{\overline{\overline{\alpha}}} = \sum_{i\in\mathcal{J}_s} \mathcal{P}^{\overline{\overline{i\alpha}}}\,, \tag{6.93}$$

$$\mathbf{g}^{\overline{\alpha}} = \sum_{i\in\mathcal{J}_s} \omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\,, \tag{6.94}$$

$$\mathbf{t}^{\overline{\overline{\alpha}}} = \sum_{i\in\mathcal{J}_s}\left[\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}} - \rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right]\,, \tag{6.95}$$

$$\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} = \begin{cases}\mathbf{v}_{\alpha}^{\overline{\kappa}} & \text{if } \kappa\in\mathcal{J}_{c\alpha}^{-}\\ \mathbf{v}_{\kappa}^{\overline{\alpha}} & \text{if } \kappa\in\mathcal{J}_{c\alpha}^{+}\end{cases}\,, \tag{6.96}$$

$$\overset{\kappa\to\alpha}{\mathbf{T}} = \sum_{i\in\mathcal{J}_s}\sum_{j\in\mathcal{J}_s}\left(\overset{j\kappa\to i\alpha}{\mathbf{T}} + \delta_{ij}\overset{i\kappa\to i\alpha}{M}\,\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\,, \tag{6.97}$$

$$\overset{\kappa\to\alpha}{\mathbf{T}^{*}} = \sum_{i\in\mathcal{J}_s}\sum_{j\in\mathcal{J}_s} \overset{j\kappa\to i\alpha}{\mathbf{T}^{*}} = \begin{cases}\langle\mathbf{t}_{\alpha}^{*}\cdot\mathbf{n}_{\alpha}\rangle_{\Omega_{\kappa},\Omega} & \text{if } \dim\kappa < \dim\alpha\\ -\langle\mathbf{t}_{\kappa}^{*}\cdot\mathbf{n}_{\kappa}\rangle_{\Omega_{\alpha},\Omega} & \text{if } \dim\kappa > \dim\alpha\end{cases}\,, \tag{6.98}$$

and

$$\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}} = \mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\,. \tag{6.99}$$

The material derivative form of the phase momentum conservation equation is obtained directly from Eq. (6.92) after applying the product rule to the second term as

$$\begin{aligned}\mathcal{P}_{*}^{\overline{\overline{\alpha}}} :=& \frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\right) + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}} - \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{M}\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} \\ &- \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{\mathbf{T}} - \frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{-}} \overset{\kappa\to\alpha}{\mathbf{T}^{*}} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right) = \mathbf{0} \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{P}}\,. \quad (6.100)\end{aligned}$$

Equations (6.92) and (6.100) are readily accessible from Table 6.3.

6.5.3 Conservation of Energy

The conservation of energy equation for a species in a phase can be derived using an approach similar to that used for deriving equations of conservation of mass and momentum. The microscale conservation of energy equation that provides the starting point is $\mathcal{E}_{i\alpha}$, Eq. (2.31). This equation is also available from Table 2.1. Application of the averaging operator $\langle\cdot\rangle_{\Omega_\alpha,\Omega}$ to this equation yields

$$\begin{aligned}\langle\mathcal{E}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} =& \left\langle \frac{\partial}{\partial t}\left(E_{i\alpha} + \rho_\alpha\omega_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right)\right\rangle_{\Omega_\alpha,\Omega} \\ &+ \left\langle \nabla\cdot\left[\left(E_{i\alpha} + \rho_\alpha\omega_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right)\mathbf{v}_{i\alpha}\right]\right\rangle_{\Omega_\alpha,\Omega} \\ &- \langle\rho_\alpha\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \langle h_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \left\langle\nabla\cdot\left(\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\cdot\mathbf{v}_{i\alpha} + \mathbf{q}_{i\alpha}\right)\right\rangle_{\Omega_\alpha,\Omega} \\ &- \langle e_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \langle\mathbf{p}_{i\alpha}\cdot\mathbf{v}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \left\langle r_{i\alpha}\frac{\mathbf{v}_{i\alpha}\cdot\mathbf{v}_{i\alpha}}{2}\right\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{P}}\,. \\ &\qquad (6.101)\end{aligned}$$

Averaging theorem T[3,(3,0),0] is applied to the time derivative, and D[3,(3,0),0] is applied to the two divergence terms. Macroscale quantities are then defined in the resultant equations that are consistent with those obtained previously. Additionally, some new macroscale quantities are defined. While the steps are similar to those previously used, the energy equation is the most complicated of the conservation equations. Therefore, the manipulations needed to produce the desired forms, while similar in nature to those already illustrated, are somewhat longer. Completion of the necessary manipulations provides the macroscale equation

$$\mathcal{E}^{i\alpha} := \frac{\partial}{\partial t}\left[E^{\overline{\overline{i\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\frac{\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}}{2} + K_E^{\overline{\overline{i\alpha}}}\right)\right]$$

$$
\begin{aligned}
&+\nabla\cdot\left\{\left[E^{\overline{\overline{i\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\frac{\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}}{2}+K_E^{\overline{\overline{i\alpha}}}\right)\right]\mathbf{v}^{\overline{i\alpha}}\right\}-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}\\
&-\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{i\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}h^{i\alpha}-\sum_{\kappa\in\mathcal{J}_{c\alpha}}\overset{i\kappa\to i\alpha}{M}\left(\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}+\frac{\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}}{2}+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}\right)\\
&-\sum_{\kappa\in\mathcal{J}_{c\alpha}}\sum_{j\in\mathcal{J}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{i\alpha,j\kappa}}}-\sum_{\kappa\in\mathcal{J}_{c\alpha}}\sum_{j\in\mathcal{J}_s}\overset{j\kappa\to i\alpha}{Q}\\
&-\frac{1}{2}\sum_{\beta\in\mathcal{J}_{c\alpha}^-}\sum_{\kappa\in\mathcal{J}_{c\beta}^-}\sum_{j\in\mathcal{J}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}^*}\cdot\mathbf{v}_{i\alpha}^{\overline{\kappa}}-\frac{1}{2}\sum_{\beta\in\mathcal{J}_{c\alpha}^-}\sum_{\kappa\in\mathcal{J}_{c\beta}^-}\sum_{j\in\mathcal{J}_s}\overset{j\kappa\to i\alpha}{Q^*}\\
&-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\cdot\mathbf{v}^{\overline{i\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{i\alpha}}}\right)\\
&-\varepsilon^{\overline{\overline{\alpha}}}e^{\overline{\overline{i\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\mathbf{p}^{\overline{\overline{i\alpha}}}\cdot\mathbf{v}^{\overline{i\alpha}}-\varepsilon^{\overline{\overline{\alpha}}}r^{i\alpha}\left(\frac{\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}}{2}+K_E^{\overline{\overline{i\alpha}}}\right)=0\quad\text{for }\alpha\in\mathcal{J}_{\mathrm{P}}\,. \qquad (6.102)
\end{aligned}
$$

We have made use of Eq. (3.170) which relates the microscale partial mass energy, $\overline{E}_{i\alpha}$, to the species energy per volume, with $E_{i\alpha}=\rho_\alpha\omega_{i\alpha}\overline{E}_{i\alpha}$. In Eq. (6.102), the new unique macroscale variables are defined as

$$E^{\overline{\overline{i\alpha}}}=\langle E_{i\alpha}\rangle_{\Omega_\alpha,\Omega}\,, \qquad (6.103)$$

$$h^{\overline{\overline{i\alpha}}}=\left\langle\rho_\alpha\omega_{i\alpha}\left(\mathbf{g}_{i\alpha}-\mathbf{g}^{\overline{i\alpha}}\right)\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega_\alpha}\,, \qquad (6.104)$$

$$\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}=\begin{cases}\overline{E}_{i\alpha}^{\overline{\kappa}} & \text{if }\kappa\in\mathcal{J}_{c\alpha}^-\\ \overline{E}_{i\kappa}^{\overline{\alpha}} & \text{if }\kappa\in\mathcal{J}_{c\alpha}^+\end{cases}\,, \qquad (6.105)$$

$$\mathbf{v}^{\overline{\overline{i\alpha,j\kappa}}}=\begin{cases}\mathbf{v}_{i\alpha}^{\overline{\kappa}} & \text{if }\kappa\in\mathcal{J}_{c\alpha}^-\\ \mathbf{v}_{j\kappa}^{\overline{\alpha}} & \text{if }\kappa\in\mathcal{J}_{c\alpha}^+\end{cases}\,, \qquad (6.106)$$

$$K_{Ei\alpha}=\frac{1}{2}\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)\,, \qquad (6.107)$$

$$K_{Ei\alpha\kappa}=\begin{cases}\frac{1}{2}\left(\mathbf{v}_{i\alpha}-\mathbf{v}_{i\alpha}^{\overline{\kappa}}\right)\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}_{i\alpha}^{\overline{\kappa}}\right) & \text{if }\kappa\in\mathcal{J}_{c\alpha}^-\\ \frac{1}{2}\left(\mathbf{v}_{i\kappa}-\mathbf{v}_{i\kappa}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_{i\kappa}-\mathbf{v}_{i\kappa}^{\overline{\alpha}}\right) & \text{if }\kappa\in\mathcal{J}_{c\alpha}^+\end{cases}\,, \qquad (6.108)$$

$$K_E^{\overline{\overline{i\alpha}}}=\frac{1}{2}\left\langle\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega_\alpha,\rho_\alpha\omega_{i\alpha}}\,, \qquad (6.109)$$

$$K_{Ei}^{\overline{\overline{\alpha,\kappa}}}=\begin{cases}K_{Ei\alpha}^{\overline{\overline{\kappa}}}=\langle K_{Ei\alpha\kappa}\rangle_{\Omega_\kappa,\Omega_\kappa,\rho_\kappa\omega_{i\kappa}} & \text{if }\kappa\in\mathcal{J}_{c\alpha}^-\\ K_{Ei\kappa}^{\overline{\overline{\alpha}}}=\langle K_{Ei\alpha\kappa}\rangle_{\Omega_\alpha,\Omega_\alpha,\rho_\alpha\omega_{i\alpha}} & \text{if }\kappa\in\mathcal{J}_{c\alpha}^+\end{cases}\,, \qquad (6.110)$$

$$\mathbf{q}^{\overline{\overline{i\alpha}}}=\Bigg\langle\mathbf{q}_{i\alpha}+\mathbf{t}_{i\alpha}{}^{\mathrm{T}}\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)-\rho_\alpha\omega_{i\alpha}\Bigg[\overline{E}_{i\alpha}-\overline{E}^{\overline{i\alpha}}$$

$$+\frac{\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)}{2}-K_E^{\overline{\overline{i\alpha}}}\Bigg]\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)\Bigg\rangle_{\Omega_\alpha,\Omega_\alpha}, \tag{6.111}$$

and

$$e^{\overline{\overline{i\alpha}}}=\Bigg\langle e_{i\alpha}+\mathbf{p}_{i\alpha}\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right) \\ +r_{i\alpha}\left[\frac{\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}^{\overline{i\alpha}}\right)}{2}-K_E^{\overline{\overline{i\alpha}}}\right]\Bigg\rangle_{\Omega_\alpha,\Omega_\alpha}. \tag{6.112}$$

The new exchange term, $\overset{j\kappa\to i\alpha}{Q}$, is defined with dim κ <dim α, as is the case here for a phase, as

$$\overset{j\kappa\to i\alpha}{Q}=\Bigg\langle\Bigg\{\underset{j\kappa\to i\alpha}{z_Q}\mathbf{q}_{i\alpha}+\underset{j\kappa\to i\alpha}{z_T}\left(\mathbf{v}_{i\alpha}-\mathbf{v}_{i\alpha}^{\overline{\kappa}}\right)\cdot\mathbf{t}_{i\alpha}+\delta_{ij}\rho_\alpha\omega_{i\alpha}\left(\mathbf{v}_\kappa-\mathbf{v}_{i\alpha}\right) \\ \times\left[\overline{E}_{i\alpha}+\frac{\left(\mathbf{v}_{i\alpha}-\mathbf{v}_{i\alpha}^{\overline{\kappa}}\right)\cdot\left(\mathbf{v}_{i\alpha}-\mathbf{v}_{i\alpha}^{\overline{\kappa}}\right)}{2}-\left(\overline{E}_{i\alpha}^{\overline{\kappa}}+K_{Ei\alpha}^{\overline{\overline{\kappa}}}\right)\right]\Bigg\}\cdot\mathbf{n}_\alpha\Bigg\rangle_{\Omega_\kappa,\Omega}, \tag{6.113}$$

subject to

$$\sum_{j\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{z_Q}=1\,. \tag{6.114}$$

If dim κ >dim α, as can occur with an interface or common curve exchanging energy with a higher-dimensional entity, then

$$\overset{j\kappa\to i\alpha}{Q}=-\Bigg\langle\Bigg\{\underset{j\kappa\to i\alpha}{z_Q}\mathbf{q}_{j\kappa}+\underset{j\kappa\to i\alpha}{z_T}\left(\mathbf{v}_{j\kappa}-\mathbf{v}_{j\kappa}^{\overline{\alpha}}\right)\cdot\mathbf{t}_{j\kappa}+\delta_{ij}\rho_\kappa\omega_{i\kappa}\left(\mathbf{v}_\alpha-\mathbf{v}_{i\kappa}\right) \\ \times\left[\overline{E}_{i\kappa}+\frac{\left(\mathbf{v}_{i\kappa}-\mathbf{v}_{i\kappa}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_{i\kappa}-\mathbf{v}_{i\kappa}^{\overline{\alpha}}\right)}{2}-\left(\overline{E}_{i\kappa}^{\overline{\alpha}}+K_{Ei\kappa}^{\overline{\overline{\alpha}}}\right)\right]\Bigg\}\cdot\mathbf{n}_\kappa\Bigg\rangle_{\Omega_\alpha,\Omega}, \tag{6.115}$$

and

$$\sum_{i\in\mathfrak{I}_s}\underset{j\kappa\to i\alpha}{z_Q}=1\,. \tag{6.116}$$

For the concentrated exchange, $\overset{j\kappa\to i\alpha}{Q^*}$, the latter part of these definitions that are multiplied by δ_{ij} are not considered here as they would be associated with concentrated inter-entity mass exchange.

Note that $h^{\overline{\overline{i\alpha}}}$ is an apparent body source of energy at the macroscale due to subscale velocity fluctuations when the external body force per mass, $\mathbf{g}_{i\alpha}$, is species-dependent. When the only external body force per mass is gravity, this term will be zero. The exchange terms account for energy transfer due to phase change ($\overset{i\kappa\to i\alpha}{M}$), transfer due to mechanical interaction between the α phase and the interface ($\overset{i\kappa\rightarrow i\alpha}{\mathbf{T}}$), and heat exchange ($\overset{i\kappa\rightarrow i\alpha}{Q}$). The concentrated energy exchange terms are included here as well. The concentrated heat conduction between a phase and the common curve will typically be negligible, but the mechanical interaction terms can be useful if one is trying to model mechanical conditions at a common curve thoroughly. The other terms defined have close analogues in the microscale equation. Because the boundary of the phase exists within the region of interest, effects at the boundary become part of the energy equation at the macroscale rather than boundary conditions for the microscale representation.

The material derivative form of energy conservation may be obtained from Eq. (6.102) as

$$\begin{aligned}
\mathcal{E}_{*}^{\overline{\overline{i\alpha}}} :=& \frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t}\left[E^{\overline{\overline{i\alpha}}} + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\frac{\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}}{2} + K_E^{\overline{\overline{i\alpha}}}\right)\right] \\
&+ \left[E^{\overline{\overline{i\alpha}}} + \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\frac{\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}}{2} + K_E^{\overline{\overline{i\alpha}}}\right)\right]\mathsf{I}{:}\mathbf{d}^{\overline{\overline{i\alpha}}} - \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}} \\
&- \epsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{i\alpha}}} - \epsilon^{\overline{\overline{\alpha}}}h^{i\alpha} - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}} \overset{i\kappa\rightarrow i\alpha}{M}\left(\overline{E}_i^{\overline{\overline{\alpha,\kappa}}} + \frac{\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}_i^{\overline{\overline{\alpha,\kappa}}}}{2} + K_{Ei}^{\overline{\overline{\alpha,\kappa}}}\right) \\
&- \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\sum_{j\in\mathfrak{J}_s} \overset{j\kappa\rightarrow i\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{i\alpha,j\kappa}}} - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\sum_{j\in\mathfrak{J}_s} \overset{j\kappa\rightarrow i\alpha}{Q} \\
&- \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}}\sum_{j\in\mathfrak{J}_s} \overset{j\kappa\rightarrow i\alpha}{\mathbf{T}^{*}}\cdot\mathbf{v}_{i\alpha}^{\overline{\kappa}} - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}}\sum_{j\in\mathfrak{J}_s} \overset{j\kappa\rightarrow i\alpha}{Q^{*}} \\
&- \nabla\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\cdot\mathbf{v}^{\overline{i\alpha}} + \epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{i\alpha}}}\right) \\
&- \epsilon^{\overline{\overline{\alpha}}}e^{\overline{\overline{i\alpha}}} - \epsilon^{\overline{\overline{\alpha}}}\mathbf{p}^{\overline{\overline{i\alpha}}}\cdot\mathbf{v}^{\overline{i\alpha}} - \epsilon^{\overline{\overline{\alpha}}}r^{i\alpha}\left(\frac{\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}}{2} + K_E^{\overline{\overline{i\alpha}}}\right) = 0 \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{P}}\,. \qquad (6.117)
\end{aligned}$$

The elements of Eqs. (6.102) and (6.117) are collected in Table 6.2 with alternative notation used to express the exchange terms as averages of microscale quantities.

For most applications, it is sufficient to solve for the energy of an entity as a whole rather than for the energy of the species that comprise the entity. To derive the energy equation for a phase, either of two approaches can be taken. One option is to average the microscale conservation of energy equation for a phase, Eq. (2.32), to the macroscale and simplify using theorems T[3,(3,0),0] and D[3,(3,0),0]. The second option is to start with Eq. (6.102), describing species conservation of energy, and sum this equation over all species. Either approach must lead to the same result. Because certain groupings of terms appear as derived quantities, care must be taken in the definition of defined quantities to ensure that the two derivation methods do indeed provide variables that are defined identically in the equation obtained.

The conservation of energy equation for a phase can thus be written as

$$
\begin{aligned}
\mathcal{E}^{\overline{\overline{\alpha}}} :=& \frac{\partial}{\partial t}\left[E^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2} + K_E^{\overline{\overline{\alpha}}}\right)\right] \\
&+ \nabla\cdot\left\{\left[E^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2} + K_E^{\overline{\overline{\alpha}}}\right)\right]\mathbf{v}^{\overline{\alpha}}\right\} - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}} \\
&- \varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}h^{\alpha} - \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}} + \frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}}{2} + K_E^{\overline{\overline{\alpha,\kappa}}}\right) \\
&- \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{Q} - \frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}}\ \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{-}} \overset{\kappa\to\alpha}{\mathbf{T}^{*}}\cdot\mathbf{v}_{\alpha}^{\overline{\kappa}} \\
&- \frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}}\ \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{-}} \overset{\kappa\to\alpha}{Q^{*}} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}} + \varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right) = 0 \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{P}}\,. \qquad (6.118)
\end{aligned}
$$

The variables that appear for the first time in this equation are defined as

$$E^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{I}_s} E^{\overline{\overline{i\alpha}}}\,, \tag{6.119}$$

$$K_E^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{I}_s} \omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\,, \tag{6.120}$$

$$K_{E\alpha\kappa} = \begin{cases} \dfrac{1}{2}\left(\mathbf{v}_{\alpha} - \mathbf{v}_{\alpha}^{\overline{\kappa}}\right)\cdot\left(\mathbf{v}_{\alpha} - \mathbf{v}_{\alpha}^{\overline{\kappa}}\right) & \text{if } \kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{-} \\ \dfrac{1}{2}\left(\mathbf{v}_{\kappa} - \mathbf{v}_{\kappa}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}_{\kappa} - \mathbf{v}_{\kappa}^{\overline{\alpha}}\right) & \text{if } \kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+} \end{cases}\,, \tag{6.121}$$

$$K_E^{\overline{\overline{\alpha,\kappa}}} = \begin{cases} K_{E\alpha}^{\overline{\overline{\kappa}}} = \langle K_{E\alpha\kappa}\rangle_{\Omega_\kappa,\Omega_\kappa,\rho_\kappa} & \text{if } \kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{-} \\ K_{E\kappa}^{\overline{\overline{\alpha}}} = \langle K_{E\alpha\kappa}\rangle_{\Omega_\alpha,\Omega_\alpha,\rho_\alpha} & \text{if } \kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+} \end{cases}\,, \tag{6.122}$$

$$\mathbf{q}^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{I}_s}\left[\mathbf{q}^{\overline{\overline{i\alpha}}} + \mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}} - \rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\left(\overline{E}^{i\alpha} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2} + K_E^{\overline{\overline{i\alpha}}}\right)\right]\,, \tag{6.123}$$

$$h^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{I}_s}\left(h^{\overline{\overline{i\alpha}}} + \rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}\right)\,, \tag{6.124}$$

$$h^{\alpha} = \sum_{i\in\mathfrak{I}_s} h^{i\alpha}\,, \tag{6.125}$$

$$\overline{E}_{\alpha}^{\overline{\kappa}} = \sum_{i\in\mathfrak{I}_s} \omega_{i\alpha}^{i\overline{\kappa}}\overline{E}_{i\alpha}^{\overline{\kappa}}\,, \tag{6.126}$$

$$\overline{E}^{\overline{\overline{\alpha,\kappa}}} = \sum_{i\in\mathfrak{I}_s} \omega_i^{\overline{\overline{\alpha,\kappa}}}\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}\,, \tag{6.127}$$

and

$$\omega_i^{\overline{\overline{\alpha,\kappa}}} = \begin{cases} \omega_{i\alpha}^{i\overline{\kappa}}, & \text{if } \kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{-} \\ \omega_{i\kappa}^{i\overline{\alpha}}, & \text{if } \kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+} \end{cases}\,. \tag{6.128}$$

The new exchange term is

$$\begin{aligned}\overset{\kappa\to\alpha}{Q} =&\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\left\{\overset{j\kappa\to i\alpha}{Q}+\overset{j\kappa\to i\alpha}{\mathbf{T}}\cdot\mathbf{u}^{\overline{\overline{i\alpha,j\kappa}}}+\delta_{ij}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}\right.\right.\\ &\left.\left.+\frac{\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}}{2}+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}-\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}}+K_E^{\overline{\overline{\alpha,\kappa}}}\right)\right]\right\}\quad\text{for }\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}\,,\end{aligned}\tag{6.129}$$

where

$$\mathbf{u}^{\overline{\overline{i\alpha,j\kappa}}}=\mathbf{v}^{\overline{\overline{i\alpha,j\kappa}}}-\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\,.\tag{6.130}$$

The material derivative form of the phase-based total energy equation is obtained directly from Eq. (6.118) as

$$\begin{aligned}\mathcal{E}_*^{\alpha}:=&\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left[E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)\right]+\left[E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)\right]\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}\\ &-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}-\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}h^{\alpha}-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}}+\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}}{2}+K_E^{\overline{\overline{\alpha,\kappa}}}\right)\\ &-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{Q}-\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^-}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^-}\overset{\kappa\to\alpha}{\mathbf{T}^*}\cdot\mathbf{v}_{\alpha}^{\overline{\kappa}}\\ &-\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^-}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^-}\overset{\kappa\to\alpha}{Q^*}-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right)=0\quad\text{for }\alpha\in\mathfrak{I}_{\mathrm{P}}\,.\end{aligned}\tag{6.131}$$

For integrating smaller scale information into macroscale models, it is important to know macroscale variables as averages of microscale variables. For convenience, the energy exchange terms in Table 6.3 are given in forms that are equivalent to Eq. (6.129), but written explicitly as averages involving microscale exchange terms. Showing that the alternative forms are equivalent is left as an exercise.

6.5.4 Balance of Entropy

The partial derivative form of the microscale entropy balance equation for species i in phase α is provided as Eq. (2.38). Application of the averaging operator to each term yields

$$\begin{aligned}\langle\mathcal{S}_{i\alpha}\rangle_{\Omega_\alpha,\Omega}=&\left\langle\frac{\partial\eta_{i\alpha}}{\partial t}\right\rangle_{\Omega_\alpha,\Omega}+\langle\nabla\cdot(\eta_{i\alpha}\mathbf{v}_{i\alpha})\rangle_{\Omega_\alpha,\Omega}-\langle b_{i\alpha}\rangle_{\Omega_\alpha,\Omega}-\langle\nabla\cdot\boldsymbol{\varphi}_{i\alpha}\rangle_{\Omega_\alpha,\Omega}\\ =&\langle\Lambda_{i\alpha}\rangle_{\Omega_\alpha,\Omega}\qquad\text{for }\alpha\in\mathfrak{I}_{\mathrm{P}}\,.\end{aligned}\tag{6.132}$$

The contributions from other species to entropy production associated with species i, as well as the impacts of irreversible processes, are included in $\Lambda_{i\alpha}$. Averaging theorem T[3,(3,0),0] may be applied to the partial time derivative and G[3,(3,0),0] to the two divergence terms. Because $\eta_{i\alpha}$, $b_{i\alpha}$, $\eta_{i\alpha}$, and $\Lambda_{i\alpha}$ do not appear in the mass, momentum, or energy equations, the definitions of larger scale averages need not be concerned with macroscale definitions provided for the conservation equations. The macroscale entropy inequality is thus obtained as

$$\begin{aligned}\mathcal{S}^{\overline{\overline{i\alpha}}} := \frac{\partial \eta^{\overline{\overline{i\alpha}}}}{\partial t} + \nabla\cdot\left(\eta^{\overline{\overline{i\alpha}}}\mathbf{v}^{\overline{i\alpha}}\right) - \varepsilon^{\overline{\overline{\alpha}}} b^{i\alpha} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{i\kappa\to i\alpha}{M}\, \overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \sum_{j\in\mathfrak{J}_s} \overset{j\kappa\to i\alpha}{\boldsymbol{\Phi}} \\ - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{c\alpha}^-} \sum_{\kappa\in\mathfrak{J}_{c\beta}^-} \sum_{j\in\mathfrak{J}_s} \overset{j\kappa\to i\alpha}{\boldsymbol{\Phi}^*} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{i\alpha}}}\right) = \Lambda^{\overline{\overline{i\alpha}}} \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{P}}\ ,\end{aligned} \tag{6.133}$$

or, in material derivative form, as

$$\begin{aligned}\mathcal{S}_*^{\overline{\overline{i\alpha}}} := \frac{\mathrm{D}^{\overline{i\alpha}}\eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} + \eta^{\overline{\overline{i\alpha}}}\mathsf{I}{:}\mathsf{d}^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}} b^{i\alpha} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{i\kappa\to i\alpha}{M}\, \overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \sum_{j\in\mathfrak{J}_s} \overset{j\kappa\to i\alpha}{\boldsymbol{\Phi}} \\ - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{c\alpha}^-} \sum_{\kappa\in\mathfrak{J}_{c\beta}^-} \sum_{j\in\mathfrak{J}_s} \overset{j\kappa\to i\alpha}{\boldsymbol{\Phi}^*} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{i\alpha}}}\right) = \Lambda^{\overline{\overline{i\alpha}}} \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{P}}\ .\end{aligned} \tag{6.134}$$

The variables in these equations are defined according to

$$\eta^{\overline{\overline{i\alpha}}} = \langle \eta_{i\alpha}\rangle_{\Omega_\alpha,\Omega}\ , \tag{6.135}$$

$$\boldsymbol{\varphi}^{\overline{\overline{i\alpha}}} = \left\langle \boldsymbol{\varphi}_{i\alpha} - \eta_{i\alpha}\left(\mathbf{v}_{i\alpha} - \mathbf{v}^{\overline{i\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega_\alpha}\ , \tag{6.136}$$

$$\overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}} = \begin{cases} \overline{\eta}_{i\alpha}^{\overline{\kappa}} & \text{if } \kappa\in\mathfrak{J}_{c\alpha}^- \\ \overline{\eta}_{i\kappa}^{\overline{\alpha}} & \text{if } \kappa\in\mathfrak{J}_{c\alpha}^+ \end{cases}\ , \tag{6.137}$$

and

$$\Lambda^{\overline{\overline{i\alpha}}} = \langle \Lambda_{i\alpha}\rangle_{\Omega_\alpha,\Omega}\ . \tag{6.138}$$

The new exchange term, $\overset{j\kappa\to i\alpha}{\boldsymbol{\Phi}}$, with dim $\kappa <$dim α, is

$$\overset{j\kappa\to i\alpha}{\boldsymbol{\Phi}} = \left\langle \left[\underset{j\kappa\to i\alpha}{z_{\Phi}}\, \boldsymbol{\varphi}_{i\alpha} + \delta_{ij}\rho_\alpha\omega_{i\alpha}\left(\overline{\eta}_{i\alpha} - \overline{\eta}_{i\alpha}^{\overline{\kappa}}\right)\left(\mathbf{v}_\kappa - \mathbf{v}_{i\alpha}\right)\right]\cdot\mathbf{n}_\alpha \right\rangle_{\Omega_\kappa,\Omega}\ , \tag{6.139}$$

and

$$\sum_{j\in\mathfrak{J}_s} \underset{j\kappa\to i\alpha}{z_{\Phi}} = 1\ . \tag{6.140}$$

If dim $\kappa >$dim α,

$$\overset{j\kappa\to i\alpha}{\boldsymbol{\Phi}} = -\left\langle \left[\underset{j\kappa\to i\alpha}{z_{\Phi}} \boldsymbol{\varphi}_{j\kappa} + \delta_{ij}\rho_{\kappa}\omega_{j\kappa}\left(\overline{\eta}_{j\kappa} - \overline{\eta}^{\overline{\alpha}}_{j\kappa}\right)(\mathbf{v}_{\alpha} - \mathbf{v}_{j\kappa})\right] \cdot \mathbf{n}_{\kappa} \right\rangle_{\Omega_{\alpha},\Omega} , \quad (6.141)$$

and

$$\sum_{i\in\mathfrak{J}_s} \underset{j\kappa\to i\alpha}{z_{\Phi}} = 1 \, . \quad (6.142)$$

Summation of Eq. (6.133) over all species $i \in \mathfrak{J}_s$ yields the balance of entropy equation

$$\begin{aligned} \mathcal{S}^{\overline{\overline{\alpha}}} := {} & \frac{\partial \eta^{\overline{\overline{\alpha}}}}{\partial t} + \nabla\cdot\left(\eta^{\overline{\overline{\alpha}}}\mathbf{v}^{\overline{\alpha}}\right) - \varepsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{\kappa\to\alpha}{M} \, \overline{\eta}^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{\kappa\to\alpha}{\boldsymbol{\Phi}} \\ & - \frac{1}{2} \sum_{\beta\in\mathfrak{J}^{-}_{c\alpha}} \sum_{\kappa\in\mathfrak{J}^{-}_{c\beta}} \overset{\kappa\to\alpha}{\boldsymbol{\Phi}^{*}} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}}\right) = \Lambda^{\overline{\overline{\alpha}}} \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{P}} \, . \end{aligned} \quad (6.143)$$

This equation can be rearranged to the material derivative form,

$$\begin{aligned} \mathcal{S}^{\overline{\overline{\alpha}}}_{*} := {} & \frac{\mathrm{D}^{\overline{\alpha}} \eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + \eta^{\overline{\overline{\alpha}}} \mathbf{l}{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{\kappa\to\alpha}{M} \, \overline{\eta}^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{\kappa\to\alpha}{\boldsymbol{\Phi}} \\ & - \frac{1}{2} \sum_{\beta\in\mathfrak{J}^{-}_{c\alpha}} \sum_{\kappa\in\mathfrak{J}^{-}_{c\beta}} \overset{\kappa\to\alpha}{\boldsymbol{\Phi}^{*}} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}}\right) = \Lambda^{\overline{\overline{\alpha}}} \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{P}} \, . \end{aligned} \quad (6.144)$$

The entity-based unique averages and the exchange terms that appear in these last two equations are defined as follows:

$$\eta^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{J}_s} \eta^{\overline{\overline{i\alpha}}} , \quad (6.145)$$

$$b^{\alpha} = \sum_{i\in\mathfrak{J}_s} b^{i\alpha}, \quad (6.146)$$

$$\overline{\eta}^{\overline{\overline{\alpha,\kappa}}} = \sum_{i\in\mathfrak{J}_s} \omega_i^{\overline{\overline{\alpha,\kappa}}} \overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}} , \quad (6.147)$$

$$\boldsymbol{\varphi}^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{J}_s} \left(\boldsymbol{\varphi}^{\overline{\overline{i\alpha}}} - \rho^{\alpha} \omega^{i\overline{\alpha}} \overline{\eta}^{\overline{i\alpha}} \mathbf{u}^{\overline{\overline{i\alpha}}} \right) , \quad (6.148)$$

$$\Lambda^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{J}_s} \Lambda^{\overline{\overline{i\alpha}}} , \quad (6.149)$$

and

$$\overset{\kappa\to\alpha}{\boldsymbol{\Phi}} = \sum_{i\in\mathfrak{J}_s} \sum_{j\in\mathfrak{J}_s} \left[\overset{j\kappa\to i\alpha}{\boldsymbol{\Phi}} + \delta_{ij} \overset{i\kappa\to i\alpha}{M} \left(\overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}} - \overline{\eta}^{\overline{\overline{\alpha,\kappa}}} \right) \right] . \quad (6.150)$$

For the concentrated entropy exchange, if any, $\overset{\kappa\to\alpha}{\boldsymbol{\Phi}^{*}}$ will not include a mass exchange component in our exposition.

6.5.5 Body Force Potential

A microscale equation for the body force potential for a species in a phase, $\Psi_{i\alpha} = \rho_\alpha \omega_{i\alpha} \psi_{i\alpha}$, has been provided in Table 2.1. The equation for the body force potential is different from a conservation equation because it involves the impact of an externally applied force on the system behavior. The material derivative form is Eq. (2.51), and the partial derivative form follows from rearrangement of that equation or from the table. The averaging operator $\langle \cdot \rangle_{\Omega_\alpha,\Omega}$ may be applied to obtain

$$\begin{aligned}\langle \mathcal{G}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = & \left\langle \frac{\partial \Psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \langle \nabla \cdot (\Psi_{i\alpha} \mathbf{v}_{i\alpha}) \rangle_{\Omega_\alpha,\Omega} + \langle \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \\ & - \left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} - \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_\mathrm{P} \,. \end{aligned} \tag{6.151}$$

Application of the averaging operator and theorems, T[3,(3,0),0] and D[3,(3,0),0], followed by breaking products to obtain familiar or newly defined variables results in

$$\begin{aligned}\mathcal{G}^{\overline{\overline{i\alpha}}} := & \frac{\partial \Psi^{\overline{\overline{i\alpha}}}}{\partial t} + \nabla \cdot \left(\Psi^{\overline{\overline{i\alpha}}} \mathbf{v}^{\overline{i\alpha}} \right) + \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{g}^{\overline{i\alpha}} \cdot \mathbf{v}^{\overline{i\alpha}} + \varepsilon^{\overline{\overline{\alpha}}} h^{\overline{\overline{i\alpha}}} \\ & - \sum_{\kappa \in \mathcal{J}_{\mathrm{c}\alpha}} \overset{i\kappa \to i\alpha}{M} \psi_i^{\overline{\overline{\alpha},\overline{\kappa}}} - \sum_{\kappa \in \mathcal{J}_{\mathrm{c}\alpha}} \overset{i\kappa \to i\alpha}{G} - \nabla \cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_\mathbf{g}^{\overline{\overline{i\alpha}}} \right) \\ & - \left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} - \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_\mathrm{P} \,, \end{aligned} \tag{6.152}$$

where

$$\Psi^{\overline{\overline{i\alpha}}} = \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \psi^{\overline{i\alpha}} = \langle \Psi_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \,, \tag{6.153}$$

$$\mathbf{q}_\mathbf{g}^{\overline{\overline{i\alpha}}} = - \left\langle \rho_\alpha \omega_{i\alpha} \left(\psi_{i\alpha} - \psi^{\overline{i\alpha}} \right) \left(\mathbf{v}_{i\alpha} - \mathbf{v}^{\overline{i\alpha}} \right) \right\rangle_{\Omega_\alpha,\Omega_\alpha} \,, \tag{6.154}$$

and

$$\psi_i^{\overline{\overline{\alpha},\overline{\kappa}}} = \begin{cases} \psi_{i\alpha}^{\overline{\kappa}} & \text{if } \kappa \in \mathcal{J}_{\mathrm{c}\alpha}^- \\ \psi_{i\kappa}^{\overline{\alpha}} & \text{if } \kappa \in \mathcal{J}_{\mathrm{c}\alpha}^+ \end{cases} \,. \tag{6.155}$$

When $\kappa \in \mathcal{J}_{\mathrm{c}\alpha}^-$,

$$\overset{i\kappa \to i\alpha}{G} = \left\langle \left(\psi_{i\alpha} - \psi_{i\alpha}^{\overline{\kappa}} \right) \rho_\alpha \omega_{i\alpha} \left(\mathbf{v}_\kappa - \mathbf{v}_{i\alpha} \right) \cdot \mathbf{n}_\alpha \right\rangle_{\Omega_\kappa,\Omega} \,, \tag{6.156}$$

while when $\kappa \in \mathcal{J}_{\mathrm{c}\alpha}^+$,

$$\overset{i\kappa\to i\alpha}{G} = \left\langle \left(\psi_{i\kappa} - \psi_{i\kappa}^{\overline{\alpha}} \right) \rho_{\kappa} \omega_{i\kappa} \left(\mathbf{v}_{i\kappa} - \mathbf{v}_{\alpha} \right) \cdot \mathbf{n}_{\kappa} \right\rangle_{\Omega_\alpha,\Omega} . \tag{6.157}$$

The material derivative form of Eq. (6.152) is obtained by rearranging the first two terms to obtain

$$\begin{aligned} \mathcal{G}_*^{\overline{\overline{i\alpha}}} :=& \frac{\mathrm{D}^{\overline{i\alpha}} \Psi^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} + \Psi^{\overline{\overline{i\alpha}}} \mathbf{l}{:}\mathbf{d}^{\overline{\overline{i\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \mathbf{g}^{\overline{i\alpha}} \cdot \mathbf{v}^{\overline{i\alpha}} + \varepsilon^{\overline{\overline{\alpha}}} h^{\overline{\overline{i\alpha}}} \\ & - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{i\kappa\to i\alpha}{M} \psi_i^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{i\kappa\to i\alpha}{G} - \nabla\cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{i\alpha}}} \right) \\ & - \left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} - \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J}_{\mathrm{P}} . \end{aligned} \tag{6.158}$$

To obtain the phase-based equation for the gravitational potential equation, we adopt the approach of summing Eq. (6.152) over all species $i \in \mathfrak{J}_s$, which is equivalent to what will be obtained by averaging $\mathcal{G}_\alpha$, yielding

$$\begin{aligned} \mathcal{G}^{\overline{\overline{\alpha}}} :=& \frac{\partial \Psi^{\overline{\overline{\alpha}}}}{\partial t} + \nabla\cdot \left(\Psi^{\overline{\overline{\alpha}}} \mathbf{v}^{\overline{\alpha}} \right) + \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \mathbf{g}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + \varepsilon^{\overline{\overline{\alpha}}} h^{\overline{\overline{\alpha}}} - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{\kappa\to\alpha}{M} \psi^{\overline{\overline{\alpha,\kappa}}} \\ & - \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \overset{\kappa\to\alpha}{G} - \nabla\cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}} \right) - \sum_{i\in\mathfrak{J}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} \\ & - \sum_{i\in\mathfrak{J}_s} \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J}_{\mathrm{P}} , \end{aligned} \tag{6.159}$$

where

$$\mathcal{G}^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{J}_s} \mathcal{G}^{\overline{\overline{i\alpha}}} , \tag{6.160}$$

$$\Psi^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{J}_s} \Psi^{\overline{\overline{i\alpha}}} , \tag{6.161}$$

$$\psi^{\overline{\overline{\alpha,\kappa}}} = \sum_{i\in\mathfrak{J}_s} \omega_i^{\overline{\overline{\alpha,\kappa}}} \psi_i^{\overline{\overline{\alpha,\kappa}}} , \tag{6.162}$$

$$\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}} = \sum_{i\in\mathfrak{J}_s} \left(\mathbf{q}_{\mathbf{g}}^{\overline{\overline{i\alpha}}} - \rho^{\alpha} \omega^{i\overline{\alpha}} \psi^{\overline{i\alpha}} \mathbf{u}^{\overline{\overline{i\alpha}}} \right) , \tag{6.163}$$

and

$$\overset{\kappa\to\alpha}{G} = \sum_{i\in\mathfrak{J}_s} \left[\overset{i\kappa\to i\alpha}{G} + \overset{i\kappa\to i\alpha}{M} \left(\psi_i^{\overline{\overline{\alpha,\kappa}}} - \psi^{\overline{\overline{\alpha,\kappa}}} \right) \right] . \tag{6.164}$$

After rearrangement to material derivative form, Eq. (6.159) becomes

$$\mathcal{G}_*^{\overline{\overline{\alpha}}} := \frac{\mathrm{D}^{\overline{\alpha}} \Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + \Psi^{\overline{\overline{\alpha}}} \mathbf{l}{:}\mathbf{d}^{\overline{\overline{i\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \mathbf{g}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} + \varepsilon^{\overline{\overline{\alpha}}} h^{\overline{\overline{\alpha}}}$$

$$- \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \overset{\kappa \to \alpha}{M} \psi^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \overset{\kappa \to \alpha}{G} - \nabla \cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}} \right)$$
$$- \sum_{i \in \mathfrak{I}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} - \sum_{i \in \mathfrak{I}_s} \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{P} \,. \tag{6.165}$$

Note that in entering the last two terms into Tables 6.2 and 6.3, use is made of a notation involving the number of primes associated with the time derivative. The exponent (n) is equal to zero for the case of a three-dimensional phase for which $\mathsf{I}_\alpha^{(0)} = \mathsf{I}_\alpha = \mathsf{I}$. The reason for introducing this notation will become apparent subsequently.

6.6 On the Forms of Macroscale Equations

At this point, having completed the derivation of the conservation and balance equations for phases at the macroscale, it is tempting to simply charge ahead to obtain the equations for interfaces, common curves, and even common points. However, it is prudent instead to pause for a moment and consider the implications of the last section.

The character of the macroscale is such that one is unable to distinguish microscale features such as the distribution of interfaces and phases. Rather, a macroscale point is somewhat of a black box within which conservation of properties associated with different species and entities may be described. From this perspective, it is reasonable, if not essential, to expect that the descriptions of conservation of properties of phases should be the same as those for interfaces. For example, mass conservation describes the amount of mass associated with a phase or interface contained within the averaging volume. If one is denied the opportunity to investigate processes at a smaller scale, the conservation equations should take the same forms. Thus the equation describing the amount of mass per total volume, plus the net outward flux, minus the rate of generation, minus the mass transferred to adjacent entities should be the same regardless of the entity with which the mass is associated. Note that this is not the case at the microscale when differential operators act in three-, two-, one-, or zero-dimensional space, depending on the entity.

The microscale conservation equations for phases, interfaces, and common curves were given in Tables 2.1–2.6. Subsequent discussion suggested how corresponding equations for common points could be deduced from these results. A general form of the microscale equations was provided in partial derivative form as Eq. (2.120) and in material derivative form as Eq. (2.121). The general forms, however, are built on different partial time derivatives and divergence operators. Transfer of these equations to a larger scale makes use of averaging theorems that are different depending on the dimensionality of the microscale equations being averaged. Besides facilitating the scale change, these theorems should, perhaps remarkably, eliminate the differences among the equation forms due to entity type, so that equations for all entities will appear the same. This occurs because entity type is not observable from the macroscale perspective. Thinking along these lines provides a fast track to the species- and entity-based equations. We can simply use the equations that appear in Tables 6.2 and 6.3 with appropriate definitions of the entity densities, $\varepsilon^{\overline{\overline{\alpha}}}$, and of the mass densities.

There are only three instances where explicit knowledge of entity type is required. The first instance is in the average of the generation terms, $G_{\Omega}^{\overline{\overline{i\alpha}}}$, for the body force potential. For this average, the partial time derivative is constrained to have fixed entity coordinates and the unit tensor components tangent to the entity, $\mathbf{I}_{\alpha}^{(n)}$, are indicated. At the macroscale, if the averaging were completed, these indicators would drop out. The second instance is in the appearance of the concentrated flux exchange terms in the momentum, energy, and entropy equations. These are the exchange terms with an asterisk. The existence of these discontinuities at common points will be excluded such that similar terms that would appear at the common points for an interface equation are zero. We do have to account for the concentrated flux term as it impacts the common curve equations. The third instance relates to the fact that the connected sets of phases consist only of interfaces. Interfaces have connected sets that consist of the two phases on each side along with the common curves that form the boundary. Common curves have both surfaces and common points as connected sets. Common points have only common curves as connected sets. Thus, in expanding out the summations over $\kappa \in \mathfrak{I}_{c\alpha}$, it is important to know the entities over which the summations are carried out. These terms account for the way that entities interact and thus describe the essential general configuration of the system.

Because averaging to the macroscale obscures the microscale dimensional character of the entities, the equations that result for the various entities are identical except for the exchange terms. Thus the averaging operations applied to the interfaces and common curves can be bypassed simply by writing down the result based on examination of the averaged phase equations. Nevertheless, in the next section we will outline the averaging procedure for an interface, and in the subsequent section for a common curve. This serves to confirm our expectations.[4]

Before becoming too euphoric over the fact that the detailed calculations of Sect. 6.5 for phases need not be repeated for other entities, one should be aware that it is the general forms of the conservation equations that are entity-independent. A significant amount of work remains to determine closure forms for $S_{\Omega}^{\overline{\overline{i\alpha}}}$ and $\mathbf{S}_{\Gamma}^{\overline{\overline{i\alpha}}}$ for species-based formulations or for $S_{\Omega}^{\overline{\overline{\alpha}}}$ and $\mathbf{S}_{\Gamma}^{\overline{\overline{\alpha}}}$ for entity-based formulations. Indeed, proper use of the expressions in the tables for all entities in conjunction with a thermodynamic framework that leads to a systematic closure procedure is quite challenging. However, we can take solace in the fact that the hard work needed to

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[4] An alternative way to confirm the generality of the form of the macroscale equation is to apply the general forms of the averaging theorems given as Eqs. (B.74) and (B.75) to the general form of the balance equation in Eq. (2.120). It will be seen that the resulting macroscale equation is independent of the dimensionality of the microscale equation.

obtain the general conservation and balance equations at the macroscale is essentially completed just by working on the phase equations.

6.7 Macroscale Principles for an Interface

The goal of this section is to confirm that the macroscale equations derived for a phase in Tables 6.2 and 6.3 apply to an interface as well. The derivations will be independent of those which lead to the equations in the table, thus confirming that the table provides general results. The approach is to begin with an interface microscale conservation equation, apply theorems T[2,(3,0),0] and D[2,(3,0),0], break averages of products into products of average quantities, and rearrange the equation to a final form. The entity-based equation can be obtained either by averaging the corresponding microscale entity-based equation or by summing the species based form.

Macroscale interface equations account, in an averaged sense, for variations in physicochemical properties rooted in molecular interactions that occur near the boundaries of two phases. Conceptually, interfaces do not occupy volume, but the conservation equations account for excess mass, momentum, energy, potential, and entropy that is assigned to the boundary between the phases. For example, physically significant quantities such as interfacial tension and interface orientation are manifestations of interfacial quantities of relevance to the formulation of macroscale models. After averaging, interfacial quantities are expressed as the relevant quantity per volume of the system. The extent of the interface is the area per volume, or the specific interfacial area.

6.7.1 Example: Conservation of Species Mass

The conservation of mass equation is the simplest expression, so we will use this equation as a starting point to demonstrate the derivation procedure for conversion of microscale interface equations to the macroscale. By formulating the conservation of mass equation for an interface in detail, we will demonstrate the process taken to derive all of the macroscale interface equations. Consider an interface between phases designated as the α interface. The connected set for a microscale point on the interface consists of the phases on each side. For example, when $\alpha = ws$, where the w phase is on one side of the interface and the s phase is on the other side, the connected set consists of the two phases such that $\mathcal{I}_{\mathrm{cws}} \cap \mathcal{I}_{\mathrm{P}} = \mathcal{I}^{+}_{\mathrm{c}ws} = \{w, s\}$. From a microscale perspective, this is the complete connected set that needs to be considered. However, from a macroscale perspective, the boundary edge of the interface is also part of the connected set. These edges are formed by common curves. At the microscale, boundary conditions for the interface are specified at the common curve. From a macroscale perspective, the common curves are entities that interact with interfaces, as do phases. Thus, from a macroscopic perspective, if three or more phases are present such that a common curve can exist, the common curve is counted as part of the connected set of entities and is obtained as $\mathcal{J}_{c\alpha}^{-} = \mathcal{J}_{c\alpha} \cap \mathcal{J}_{\mathrm{C}}$ for $\alpha \in \mathcal{J}_{\mathrm{I}}$. Thus, continuing the example, if the *ws* interface exists in a system composed of *w*, *n*, and *s* phases, the connected set for the *ws* interface is $\mathcal{J}_{\mathrm{c}ws} = \mathcal{J}_{\mathrm{c}ws}^{+} \cup \mathcal{J}_{\mathrm{c}ws}^{-} = \{w, s, wns\}$. In other words, for the microscale equations of Chap. 2, connected sets of importance are of one-dimension higher than the entity of interest. Phases have no connected sets; interfaces are in the connected sets of a common curve. However, from a macroscale perspective, connected sets to an entity are adjacent entities of both one higher dimension and one lower dimension. Interfaces are important parts of the connected sets of phases; both phases and common curves are important members of the connected sets of interfaces.

Consider an interface in domain Ω_α between two phases such that the species conservation of mass equation, $\mathcal{M}_{i\alpha}$, is given by Eq. (2.71) or can be obtained from Table 2.3. Application of the averaging operator $\langle\cdot\rangle_{\Omega_\alpha,\Omega}$ to this equation yields

$$\begin{aligned}\langle \mathcal{M}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} = &\left\langle \frac{\partial'(\rho_\alpha \omega_{i\alpha})}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \nabla' \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}) \right\rangle_{\Omega_\alpha,\Omega} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^{+}} \left\langle \underset{i\kappa \to i\alpha}{M} \right\rangle_{\Omega_\alpha,\Omega} \\ &- \langle r_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_{\mathrm{I}} \, . \end{aligned} \tag{6.166}$$

Implementation of theorem T[2,(3,0),0] to rearrange the time derivative and theorem D[2,(3,0),0] to rearrange the surface divergence term yields

$$\begin{aligned}\langle \mathcal{M}_{i\alpha}\rangle_{\Omega_\alpha,\Omega} = &\frac{\partial \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \right)}{\partial t} + \nabla \cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) - \sum_{\kappa \in \mathcal{J}_{c\alpha}^{+}} \left\langle \underset{i\kappa \to i\alpha}{M} \right\rangle_{\Omega_\alpha,\Omega} \\ &- \varepsilon^{\overline{\overline{\alpha}}} r^{i\alpha} + \sum_{\kappa \in \mathcal{J}_{c\alpha}^{-}} \langle \rho_\alpha \omega_{i\alpha} (\mathbf{v}_{i\alpha} - \mathbf{v}_\kappa) \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} = 0 \, . \end{aligned} \tag{6.167}$$

The two exchange terms in this expression have been defined previously in Eq. (6.50) and using the inter-entity exchange term notation in the bottom part of Table 6.2. Since α refers to an interface entity, $\dim \alpha = 2$. When $\kappa \in \mathcal{J}_{c\alpha}^{+}$, κ refers to a phase, but when $\kappa \in \mathcal{J}_{c\alpha}^{-}$, κ refers to a common curve. Therefore the transfer of mass of species i to the α interface is accounted for by the two exchange terms with

$$\overset{i\kappa \to i\alpha}{M} = \langle \rho_\alpha \omega_{i\alpha} (\mathbf{v}_\kappa - \mathbf{v}_{i\alpha}) \cdot \mathbf{n}_\alpha \rangle_{\Omega_\kappa,\Omega} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^{-} \tag{6.168}$$

and

$$\overset{i\kappa \to i\alpha}{M} = \left\langle \underset{i\kappa \to i\alpha}{M} \right\rangle_{\Omega_\alpha,\Omega} \qquad \text{for } \kappa \in \mathcal{J}_{c\alpha}^{+} \, . \tag{6.169}$$

Substitution of these last two relations into Eq. (6.167) gives

$$\langle \mathcal{M}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = \frac{\partial \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \right)}{\partial t} + \nabla \cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) - \varepsilon^{\overline{\overline{\alpha}}} r^{i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \overset{i\kappa \to i\alpha}{M} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^-} \overset{i\kappa \to i\alpha}{M} = 0 \,. \tag{6.170}$$

However the summations over the phase and over the common curve can be combined as a single sum over the complete connected set of α, $\mathcal{J}_{c\alpha}$. Therefore, with

$$\sum_{\kappa \in \mathcal{J}_{c\alpha}} \overset{i\kappa \to i\alpha}{M} = \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \overset{i\kappa \to i\alpha}{M} + \sum_{\kappa \in \mathcal{J}_{c\alpha}^-} \overset{i\kappa \to i\alpha}{M} \,, \tag{6.171}$$

Equation (6.170) may be rewritten

$$\mathcal{M}^{\overline{\overline{i\alpha}}} := \frac{\partial \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \right)}{\partial t} + \nabla \cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) - \varepsilon^{\overline{\overline{\alpha}}} r^{i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \overset{i\kappa \to i\alpha}{M} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_{\mathrm{I}} \,. \tag{6.172}$$

Equation (6.172) is identical in form to the species conservation equation obtained for a phase α as given by Eq. (6.48). In the interface equation, ρ^α has units of mass per area; $\varepsilon^{\overline{\overline{\alpha}}}$ is area per volume such that $\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha$ is mass per averaging volume associated with interface entity α. In Eq. (6.48), ρ^α is mass per volume of phase α and $\varepsilon^{\overline{\overline{\alpha}}}$ is the volume of phase entity α per averaging volume. Similarly, $r^{i\alpha}$ is the macroscopic rate of generation of species i per extent of entity α. If one keeps these notational distinctions in mind, the equations are identical in appearance. Note also that since both the phase and interface equation have dimensions of mass per volume, the two equations can be added together to express the total mass conservation in the phase and interface being considered per unit volume. Of course, if these equations are added, it is simpler to designate the phase using one index and the interface using another. Typically, when we want to make such a distinction, we choose a single index for the phase, such as $\alpha = w$ for a wetting fluid phase, and a double index for the interface, such as $\alpha = ws$ for the interface between a w and s phase. This kind of distinction becomes useful when considering the system as a whole, as in the development of closure relations, and was employed previously in Table 4.1 in developing variational relations. For now, we simply note that Eq. (6.172), the expression for conservation of mass of a species i in an interface α, can be extended to apply to any entity in the system with

$$\mathcal{M}^{\overline{\overline{i\alpha}}} := \frac{\partial \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \right)}{\partial t} + \nabla \cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mathbf{v}^{\overline{i\alpha}} \right) - \varepsilon^{\overline{\overline{\alpha}}} r^{i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}} \overset{i\kappa \to i\alpha}{M} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J} \,. \tag{6.173}$$

The only difference between this equation and Eqs. (6.172) and (6.48) is the extension of the set of domains to which it applies to include common curves and common points. Thus, the mass conservation equation in Table 6.2, based on analysis of a phase entity, applies to other entities as well.

6.7.2 Comment on Interface Equations

The derivation of interface equations can proceed, if desired, by averaging the microscale equations to the macroscale. The result, as has been stated, is the set of equations in Tables 6.2 and 6.3. Because these equations are already available, and the steps to their derivation have been provided, it seems not to be worthwhile to engage in the manipulations needed to develop the equations in this text. Detailed derivations can be found elsewhere [1, 2, 7, 8] if desired. We note that definitions of unique averaged variables and conditions on variables are the same as in Eqs. (6.66)–(6.72) encountered when averaging mass conservation; Eqs. (6.78)–(6.80), (6.83)–(6.84), and (6.94)–(6.98) introduced in the context of momentum conservation; Eqs. (6.103)–(6.112) and (6.119)–(6.130) introduced when averaging the energy equation; Eqs. (6.135)–(6.138) and (6.145)–(6.149) relating to macroscale entropy balance variables; and Eqs. (6.153)–(6.154) and (6.160)–(6.163) that arise in obtaining the macroscale body force potential equation. For convenience the variables in these equations are collected in the notation section along with reference to the equation numbers where they are defined.

Although the macroscale equation formulas are universal with regard to entity, it is useful to make a few remarks about the microscale variables in the equations. One of the strengths of the TCAT method in comparison to other methods is that it retains connections between microscale and macroscale variables. Sometimes, examination of the ways that microscale variables impact the definitions of larger scale variables is useful. Whether the domain of a microscale variable is within a phase or located on an interface can be important. Failure to recognize this difference can lead to misunderstanding and errors in developing closure relations.

In Eq. (2.24), the microscale diffusion velocity is defined as

$$\mathbf{u}_{i\alpha} = \mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha} \, . \tag{6.174}$$

In a three-dimensional phase domain, diffusion can occur in all directions so that this definition provides the possibility for transport in any direction. However, in a two-dimensional domain, diffusion cannot occur in the domain in a direction normal to the domain. The velocity of all species in the direction normal to the surface must be equal to each other and to the velocity of the surface. This may be expressed as

$$\mathbf{v}_{i\alpha}\cdot\left(\mathsf{I} - \mathsf{I}'_{\alpha}\right) = \mathbf{v}_{\alpha}\cdot\left(\mathsf{I} - \mathsf{I}'_{\alpha}\right) \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{I}} \, . \tag{6.175}$$

As a consequence

$$\mathbf{u}_{i\alpha}\cdot\left(\mathsf{I} - \mathsf{I}'_{\alpha}\right) = \mathbf{0} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{I}} \, . \tag{6.176}$$

Recognition of this fact can be useful in developing closure relations for surface entities.

Another point of interest is the generation term of the body force potential equation. From Eq. (6.152) for $\alpha \in \mathfrak{J}_\mathrm{P}$ and Table 6.2, we know that

$$G_{\Omega}^{\overline{\overline{i\alpha}}} = \left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \, . \tag{6.177}$$

Here we will concentrate on the first term on the right side for the case of an interface. A time derivative fixed to a point on an interface must take into account the fact that the interface can move in a direction normal to the surface. The time derivative with surface coordinates of an interface entity α held fixed is related to the time derivative with spatial coordinates fixed according to

$$\frac{\partial}{\partial t} = \frac{\partial'}{\partial t} - \mathbf{v}_\alpha \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha \right) \cdot \nabla \, . \tag{6.178}$$

Application of this identity to the first term on the right of Eq. (6.177) produces

$$\left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial' \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha \omega_{i\alpha} \mathbf{v}_\alpha \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha \right) \cdot \nabla \psi_{i\alpha} \right\rangle_{\Omega_\alpha,\Omega} \, . \tag{6.179}$$

However, $\nabla \psi_{i\alpha} = -\mathbf{g}_{i\alpha}$ so this equation becomes

$$\left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \left\langle \rho_\alpha \omega_{i\alpha} \frac{\partial' \psi_{i\alpha}}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \rho_\alpha \omega_{i\alpha} \mathbf{v}_\alpha \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha \right) \cdot \mathbf{g}_{i\alpha} \right\rangle_{\Omega_\alpha,\Omega} \, . \tag{6.180}$$

The form on the left side of this equation is appropriate for use when $\alpha \in \mathfrak{J}_\mathrm{P}$, while the equivalent term on the right is more appropriate for $\alpha \in \mathfrak{J}_\mathrm{I}$. This change in notation is accounted for in expressing the generation term for the gravitational potential in Tables 6.2 and 6.3.

6.8 Macroscale Principles for a Common Curve

Macroscale common curve equations account in an averaged sense for variations in physicochemical properties rooted in molecular interactions that occur in the neighborhood where three phases or three interfaces meet. Although curves can be formed at the intersection of more than three phases, we will not consider these rare events in the formulation that follows. Conceptually, common curves do not occupy volume or surface area, but their conservation and balance equations account for variability of mass, momentum, energy, potential, and entropy properties that actually exist in the region of the conceptualized curve. For example, a physically significant quantity such as curvilineal tension is a manifestation of molecular behavior in the vicinity of a proposed common curve location that may be of relevance to the formulation of some macroscale models. After averaging, common curve conservation equations are expressed in terms of the rate of change of the property per averaging volume of the system that contains the common curve. The extent of the common curve in the averaging domain is expressed as the common curve length per volume, also called the specific common curve length. For an α common curve, it is denoted $\varepsilon^{\overline{\overline{\alpha}}}$. Thus, a universal notation is used to designate volume, surface, and common curve densities such that one must be careful to associate the symbol with the appropriate entity. In some instances, to make this clear, a common curve property is designated using three indices, such as $\varepsilon^{\overline{\overline{wns}}}$ which would indicate a specific common curve length associated with locations where *wn*, *ws*, and *ns* interfaces come together.

The formulation of the common curve equations follows the now familiar pattern of applying the averaging operator $\langle\cdot\rangle_{\Omega_\alpha,\Omega}$ to a microscale common curve equation of interest, rearranging the average quantities using Theorems T[1,(3,0),0] and D[1,(3,0),0], and defining the macroscale properties after breaking products as needed. The equations can be developed in terms of species-based equations, which may subsequently be summed over the species to produce the common curve entity-based equations. Alternatively, the microscale common curve equations may be averaged directly. Regardless of the approach used, the definitions of macroscale quantities are consistent.

The mechanics of this formulation have been established and demonstrated in detail for phases in Sect. 6.5 and for the species mass conservation equation of an interface in Sect. 6.7.1. Considerations of the form of the macroscale equation in Sect. 6.6 suggest the macroscale conservation equations for common curves will be identical in appearance to those for the phase equations as collected in Tables 6.2 and 6.3. Thus, although the equations for the common curves can be derived as an independent exercise, it seems prudent to forego providing the manipulations in favor of simply asserting that the results are found in the two tables. One example derivation is provided in the next subsection purely for illustrative purposes. Note that the definitions of the macroscale variables in these equations in terms of microscale precursors are independent of the entity considered. Only the averaging region is different. Additionally, if a concentrated non-advective force is exerted at a common curve on a smooth solid surface, this phenomenon must be accounted for in the macroscale common curve equation. These are the exchange terms with an asterisk that involve forces exerted by a phase on a common curve.

6.8.1 Example: Conservation of Common Curve Momentum

Consider a common curve domain, Ω_α, where three interfaces meet such that the entity-based conservation of momentum equation, $\mathcal{P}_\alpha$, is given by Eq. (2.107) or can be obtained from Table 2.6. Application of the averaging operator $\langle\cdot\rangle_{\Omega_\alpha,\Omega}$ to this equation yields

$$\begin{aligned}\langle \mathcal{P}_\alpha \rangle_{\Omega_\alpha,\Omega} = & \left\langle \frac{\partial''(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \nabla''\cdot(\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha)\right\rangle_{\Omega_\alpha,\Omega} - \langle \rho_\alpha \mathbf{g}_\alpha \rangle_{\Omega_\alpha,\Omega} \\ & - \sum_{\kappa\in\mathfrak{I}_{c\alpha}^{+}} \left\langle \mathbf{v}_\kappa \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\mathbf{T}} \right\rangle_{\Omega_\alpha,\Omega} - \frac{1}{2} \sum_{\beta\in\mathfrak{I}_{c\alpha}^{+}} \sum_{\kappa\in\mathfrak{I}_{c\beta}^{+}} \left\langle \underset{\kappa\to\alpha}{\mathbf{T}^*} \right\rangle_{\Omega_\alpha,\Omega} \\ & - \left\langle \nabla''\cdot\left(\mathbf{l}''_\alpha\cdot\mathbf{t}_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega} = \mathbf{0} \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{C}} \,. \end{aligned} \tag{6.181}$$

Theorems T[1,(3,0),0] and D[1,(3,0),0] from Table 6.1 are employed to re-express the time derivative and curve divergence terms, respectively, such that

$$\begin{aligned}\langle \mathcal{P}_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = & \frac{\partial}{\partial t}\left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{v}^{\overline{\alpha}}\right) + \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{v}^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}}\right) - \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{g}^{\overline{\alpha}} \\ & - \sum_{\kappa\in\mathfrak{I}_{c\alpha}^{+}} \left\langle \mathbf{v}_\kappa \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\mathbf{T}} \right\rangle_{\Omega_\alpha,\Omega} - \frac{1}{2} \sum_{\beta\in\mathfrak{I}_{c\alpha}^{+}} \sum_{\kappa\in\mathfrak{I}_{c\beta}^{+}} \left\langle \underset{\kappa\to\alpha}{\mathbf{T}^*} \right\rangle_{\Omega_\alpha,\Omega} \\ & + \sum_{\kappa\in\mathfrak{I}_{c\alpha}^{-}} \langle \mathbf{n}_\alpha\cdot\left[\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}_\kappa\right)\mathbf{v}_\alpha - \mathbf{t}_\alpha\right]\rangle_{\Omega_\kappa,\Omega} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}}\right) = \mathbf{0} \\ & \text{for } \alpha\in\mathfrak{I}_{\mathrm{C}} \,. \end{aligned} \tag{6.182}$$

Based on the definitions of exchange terms at the bottom of Table 6.3, Eqs. (6.50) and (6.82)–(6.85) we can see that

$$\left\langle \mathbf{v}_\kappa \underset{\kappa\to\alpha}{M} + \underset{\kappa\to\alpha}{\mathbf{T}} \right\rangle_{\Omega_\alpha,\Omega} = \overset{\kappa\to\alpha}{M} \mathbf{v}^{\overline{\overline{\alpha,\kappa}}} + \overset{\kappa\to\alpha}{\mathbf{T}} \quad \text{for } \kappa\in\mathfrak{I}_{c\alpha}^{+} \,, \tag{6.183}$$

$$\langle \mathbf{n}_\alpha\cdot\left[\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}_\kappa\right)\mathbf{v}_\alpha - \mathbf{t}_\alpha\right]\rangle_{\Omega_\kappa,\Omega} = -\overset{\kappa\to\alpha}{M} \mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \overset{\kappa\to\alpha}{\mathbf{T}} \quad \text{for } \kappa\in\mathfrak{I}_{c\alpha}^{-} \,, \tag{6.184}$$

and

$$\left\langle \underset{\kappa\to\alpha}{\mathbf{T}^*} \right\rangle_{\Omega_\alpha,\Omega} = \overset{\kappa\to\alpha}{\mathbf{T}^*} \quad \text{for } \beta\in\mathfrak{I}_{c\alpha}^{+}, \kappa\in\mathfrak{I}_{c\beta}^{+} \,. \tag{6.185}$$

Equation (6.183) accounts for exchanges between the common curve and the connected set of interfaces; Eq. (6.184) accounts for exchanges between the common curve and common points. Equation (6.185) accounts for concentrated sources that model exchanges between the common curve and a phase when the phase has a unique normal to the common curve. Substitution of Eqs. (6.183)–(6.185) back into Eq. (6.182) while combining the exchanges between the common curve and the connected sets into a single expression yields

$$\begin{aligned}\mathcal{P}^{\overline{\overline{\alpha}}} := & \frac{\partial}{\partial t}\left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{v}^{\overline{\alpha}}\right) + \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{v}^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}}\right) - \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{g}^{\overline{\alpha}} - \sum_{\kappa\in\mathfrak{I}_{c\alpha}} \overset{\kappa\to\alpha}{M} \mathbf{v}^{\overline{\overline{\alpha,\kappa}}} \\ & - \sum_{\kappa\in\mathfrak{I}_{c\alpha}} \overset{\kappa\to\alpha}{\mathbf{T}} - \frac{1}{2} \sum_{\beta\in\mathfrak{I}_{c\alpha}^{+}} \sum_{\kappa\in\mathfrak{I}_{c\beta}^{+}} \overset{\kappa\to\alpha}{\mathbf{T}^*} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}}\right) = \mathbf{0} \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{C}} \,. \end{aligned} \tag{6.186}$$

Equation (6.186) is identical in form to the phase momentum equation given as Eq. (6.92), except that a different double sum term appears. For the phase equation, a double sum occurs over a concentrated force term for an entity that is lower order by two dimensions, i.e., over a common curve property. For the common curve equation, the summation is over an entity two dimensions higher. This term accounts for the interaction of the common curve of interest with a phase. If α refers to a three-dimensional phase, no five-dimensional entity will exist so that this summation is dropped. However, for α denoting a common curve, which is microscopically one-dimensional, interaction with a phase can occur when the normal to the phase at the common curve is unique, and a concentrated force acts at that location. Thus the additional term in Eq. (6.186) accounts for this possibility where $\underset{\kappa\to\alpha}{\mathbf{T}^*}$ has been appropriately defined at the bottom of Table 2.6. Conversely, no double sum term for an entity of two dimensions lower than a common curve appears, because no such entity exists.

Similar agreement between forms of the conservation equations in various entities applies such that the equations in Tables 6.2 and 6.3 may be applied to any entity. This feature is one of the significant mathematical differences between the microscale conservation equations and their macroscale counterparts. At the microscale the dimensionality of the entity impacts the equation forms; at the macroscale, the interaction between an entity and connected and adjacent entities accounts for the differences in system behavior.

6.8.2 Comment on Common Curve Equations

Although the forms of the macroscale equations for phases, interfaces, common curves, and, for that matter, common points are identical, one should not lose sight of some of the distinguishing features of common curves that will impact closure relations. Fluxes of mass, momentum, or energy in the common curves at the microscale are only in directions tangent to the common curve. Thus, for example, if one imagines a situation where common curves are all straight lines oriented in the same direction, no non-advective heat flux will be induced in the curves by a temperature gradient that is orthogonal to the common curves. At the macroscale, the effects of average orientation of the curves in a system will be important in consideration of how the system behaves. Two systems composed of the same materials that have the same values of $\varepsilon^{\overline{\overline{\alpha}}}$ for all entities will not necessarily respond identically to an imposed external force because the subscale distribution of entities and the orientations of those entities can be different. Orientation, at least on average, must be accounted for in closure equations if common curve dynamics are to be modeled properly.

The number of entities in a porous medium system increases rapidly as the number of phases increases. Although a two-phase system has 3 entities, a three-phase system can have 7 entities, and a four-phase system can have 15 entities. Modeling the conservation equations for each chemical species in each entity is a huge task, even at the macroscale. It seems reasonable to assume that lower-dimensional entities will have less importance in accurate description of system behavior than will higher-dimensional entities. Therefore, although we can develop closed equations for common curves, it is usual to exclude the properties of common curves from a full model. In adopting this approach, one must be aware, however, that an error is incurred when this aspect of system dynamics is excluded. Although some might argue that the TCAT approach is too complex because it explicitly includes common curve dynamics in the general formulation, we believe that any model that does not include common curve dynamics should exclude them explicitly. Detail provided by the TCAT approach can help pinpoint situations where exclusion of common curve dynamics could be a significant source of error that contributes to the failure of standard models.

6.9 Mixed Forms of Macroscale Equations

The forms of the inter-entity exchange terms for both the species-based and phase-based forms of the conservation and balance equations have been provided in Tables 6.2 and 6.3. Although these forms are complete, the actual expression used in formulating a problem description often will consist of mixes of the two forms. For example, when the description of species mass conservation must be more refined than that of species momentum transport, species-based mass conservation equations can be used in conjunction with entity-based momentum equations. In instances when this type of mixed formulation is employed, the inter-entity exchange terms in entity-based equations as well as the non-advective flux terms must be revisited. Although the definitions of these terms are unchanged, it is helpful in developing closure relations to examine the components that go into the definitions. For example, rather than modeling $\overset{\kappa\to\alpha}{Q}$ as a whole as given in Eq. (6.129), it is sometimes advantageous to model the various terms that contribute to this expression separately. The implications of this concept are explored in the following subsections.

6.9.1 *Species-based Equations*

The first case is when the full set of species-based conservation equations for mass, momentum, and energy along with the body force potential and entropy balance equation are employed in describing the system, and constitutive equations are also defined on a species basis. The exchange terms will also all be species-based so that the set of exchange terms, $\mathcal{X}$, in this instance is

$$\mathcal{X} = \{ \overset{i\kappa\to i\alpha}{M}, \overset{j\kappa\to i\alpha}{\mathbf{T}}, \overset{j\kappa\to i\alpha}{Q}, \overset{j\kappa\to i\alpha}{\Phi}, \overset{i\kappa\to i\alpha}{G} \} \quad \text{for } \alpha \in \mathcal{I}; \kappa \in \mathcal{I}_{c\alpha}; i,j \in \mathcal{I}_s . \tag{6.187}$$

The definitions of these exchange quantities were given in the last section. These definitions are useful if one is interested in employing microscale experimental data to determine appropriate forms for these macroscale expressions. In actuality, these terms are typically parameterized directly at the macroscale. These efforts do not require microscale information but only seek to obtain macroscale closure relations.

6.9.2 Entity-based Energy and Entropy

A reduction in the equation set can be achieved by writing the entropy, energy, and body force potential equations in terms of entity-based quantities while leaving the momentum and mass equations in terms of species. The species-based conservation equations employed are the mass and momentum equations in Table 6.2. The entity-based energy conservation, entropy balance, and force potential equations are taken from Table 6.3. The problem with this mixed formulation is that while some quantities appear in the species-based equations as species-based properties (e.g., $\overset{i\kappa\to i\alpha}{M}$, $\overline{\overline{\mathbf{t}}}^{\overline{i\alpha}}$, $\overset{j\kappa\to i\alpha}{\mathbf{T}}$), only their entity-based forms (e.g., $\overset{\kappa\to\alpha}{M}$, $\overline{\overline{\mathbf{t}}}^{\overline{\alpha}}$, $\overset{\kappa\to\alpha}{\mathbf{T}}$) appear in the entity-based equations. Thus it is necessary to express these entity-based forms in terms of species-based variables employed in the species-based equations.

Remember that the entity-based equations are obtained as a sum of the species-based equations over the N species in the entity. Thus, for the present case, we obtain a reduction in the number of variables relating to energy, but there is no reduction in the number of variables relating to mass and momentum transfer processes. In the energy equation from Table 6.3, we replace entity-based variables by their corresponding summations as given by Eqs. (6.70), (6.94), (6.95), (6.97), and (6.98). Also, the definitions provided in Eqs. (6.119)–(6.129) are employed. This honors the species-based detail of the mass and momentum equations while still allowing the energy description to be simplified.

With these considerations, the total energy equation becomes

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left\{E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left[\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+\sum_{i\in\mathfrak{I}_s}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\right\}\\
&+\left\{E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left[\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+\sum_{i\in\mathfrak{I}_s}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\right\}\mathsf{I}{:}\mathbf{d}^{\overline{\alpha}}\\
&-\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)-\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{i\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}h^{\alpha}\\
&-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{I}_s}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}+\frac{\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)}{2}+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}\right]\\
&-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}}\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}^{\overline{\overline{i\alpha,j\kappa}}}\right)-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{Q}
\end{aligned}
$$

$$-\frac{1}{2}\sum_{\beta\in\mathfrak{I}^-_{\mathrm{c}\alpha}}\sum_{\kappa\in\mathfrak{I}^-_{\mathrm{c}\beta}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}^*}\cdot\left(\mathbf{v}_{\alpha}^{\overline{\kappa}}+\mathbf{u}_{i\alpha}^{\overline{\overline{\kappa}}}\right)-\frac{1}{2}\sum_{\beta\in\mathfrak{I}^-_{\mathrm{c}\alpha}}\sum_{\kappa\in\mathfrak{I}^-_{\mathrm{c}\beta}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{Q^*}$$

$$-\frac{1}{2}\sum_{\beta\in\mathfrak{I}^+_{\mathrm{c}\alpha}}\sum_{\kappa\in\mathfrak{I}^+_{\mathrm{c}\beta}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}^*}\cdot\left(\mathbf{v}_{\kappa}^{\overline{\alpha}}+\mathbf{u}_{i\kappa}^{\overline{\overline{\alpha}}}\right)-\frac{1}{2}\sum_{\beta\in\mathfrak{I}^+_{\mathrm{c}\alpha}}\sum_{\kappa\in\mathfrak{I}^+_{\mathrm{c}\beta}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{Q^*}$$

$$-\nabla\cdot\left\{\sum_{i\in\mathfrak{I}_s}\left[\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\cdot\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)\right]\right\}-\nabla\cdot\left\{\sum_{i\in\mathfrak{I}_s}\left[\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{i\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right.\right.$$

$$\left.\left.\times\left(\overline{E}^{\overline{i\alpha}}+\frac{\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)\cdot\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)}{2}+K_E^{\overline{\overline{i\alpha}}}\right)\right]\right\}=0\,. \tag{6.188}$$

The summations involving $\overset{j\kappa\to i\alpha}{\mathbf{T}^*}$ and $\overset{j\kappa\to i\alpha}{Q^*}$ over entities two dimensions lower than α are zero unless α is a phase (since common point singularities are being neglected); and the summations of these quantities over entities two dimensions higher are included only when $\alpha\in\mathfrak{I}_{\mathrm{C}}$.

In this equation, we can identify the following groups of terms that should each be defined for use with the entity-based energy equation:

$$\mathbf{q}_0^{\overline{\overline{\alpha}}}=\sum_{i\in\mathfrak{I}_s}\mathbf{q}^{\overline{\overline{i\alpha}}}-\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\left(\overline{E}^{\overline{i\alpha}}+\frac{\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)\cdot\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)}{2}+K_E^{\overline{\overline{i\alpha}}}\right)\,, \tag{6.189}$$

$$h_0^{\overline{\overline{\alpha}}}=\sum_{i\in\mathfrak{I}_s}h^{\overline{\overline{i\alpha}}}\,, \tag{6.190}$$

$$\overset{\kappa\to\alpha}{Q_0^*}=\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{Q^*}\quad\text{for }\beta\in\mathfrak{I}^-_{\mathrm{c}\alpha},\kappa\in\mathfrak{I}^-_{\mathrm{c}\beta}\,, \tag{6.191}$$

$$\overset{\kappa\to\alpha}{Q_0^*}=\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{Q^*}\quad\text{for }\beta\in\mathfrak{I}^+_{\mathrm{c}\alpha},\kappa\in\mathfrak{I}^+_{\mathrm{c}\beta}\,, \tag{6.192}$$

and

$$\overset{\kappa\to\alpha}{Q_0}=\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{Q}\quad\text{for }\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}\,. \tag{6.193}$$

The subscript "0" denotes that these terms are different from those defined previously without the "0". In fact, these terms are simpler than the former ones, indicative of the fact that some of the system physics is retained explicitly in the mass and momentum equations when they are not summed over all species. Thus the constitutive equations needed for Eqs. (6.189)–(6.193) should be simpler than those when all the conservation equations are formulated on an entity basis. Of course, this comes at the price of solving more momentum and mass conservation equations along with developing additional constitutive equations for quantities such as

$\mathbf{t}^{\overline{\overline{i\alpha}}}$ and $\overset{j\kappa\to i\alpha}{\mathbf{T}}$ for each species. Insertion of Eqs. (6.189)–(6.193) into Eq. (6.188) yields

$$\begin{aligned}
&\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left\{E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left[\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+\sum_{i\in\mathfrak{I}_s}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\right\}\\
&+\left\{E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left[\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+\sum_{i\in\mathfrak{I}_s}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\right\}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}\\
&-\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)-\varepsilon^{\overline{\overline{\alpha}}}h_0^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}h^{\alpha}\\
&-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{I}_s}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}+\frac{\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)}{2}+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}\right]\\
&-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}}\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}^{\overline{\overline{i\alpha,j\kappa}}}\right)-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{Q_0}\\
&-\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{-}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}^{*}}\cdot\left(\mathbf{v}_{\alpha}^{\overline{\kappa}}+\mathbf{u}_{i\alpha}^{\overline{\overline{\kappa}}}\right)-\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{-}}\overset{\kappa\to\alpha}{Q_0^{*}}\\
&-\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{+}}\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}^{*}}\cdot\left(\mathbf{v}_{\kappa}^{\overline{\alpha}}+\mathbf{u}_{i\kappa}^{\overline{\overline{\alpha}}}\right)-\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{+}}\overset{\kappa\to\alpha}{Q_0^{*}}\\
&-\nabla\cdot\left\{\sum_{i\in\mathfrak{I}_s}\left[\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}\cdot\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)\right]\right\}-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_0^{\overline{\overline{\alpha}}}\right)=0\,. \qquad (6.194)
\end{aligned}$$

Similar manipulations for the entropy balance give

$$\begin{aligned}
\mathcal{S}_{**}^{\overline{\overline{\alpha}}}=&\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\eta^{\overline{\overline{\alpha}}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}b^{\alpha}-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{I}_s}\overset{i\kappa\to i\alpha}{M}\,\overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}}-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{\Phi_0}\\
&-\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{-}}\overset{\kappa\to\alpha}{\Phi^{*}}-\frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{+}}\overset{\kappa\to\alpha}{\Phi^{*}}-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}\right)=\Lambda^{\overline{\overline{\alpha}}}\,, \qquad (6.195)
\end{aligned}$$

where

$$\overset{\kappa\to\alpha}{\Phi_0}=\sum_{i\in\mathfrak{I}_s}\sum_{j\in\mathfrak{I}_s}\overset{j\kappa\to i\alpha}{\Phi}\,. \qquad (6.196)$$

For the body force potential, we obtain

$$\mathcal{G}_{**}^{\overline{\overline{\alpha}}}=\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\Psi^{\overline{\overline{\alpha}}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)+\varepsilon^{\overline{\overline{\alpha}}}h_0^{\overline{\overline{\alpha}}}$$

$$
\begin{aligned}
&- \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \overset{i\kappa\to i\alpha}{M} \psi_i^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa \in \mathfrak{I}_{c\alpha}} \sum_{i \in \mathfrak{I}_s} \overset{\kappa\to\alpha}{G_0} - \nabla\cdot \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}} - \sum_{i \in \mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \psi^{\overline{i\alpha}} \mathbf{u}^{\overline{\overline{i\alpha}}} \right) \\
&- \sum_{i \in \mathfrak{I}_s} \left\langle \rho_\alpha \omega_{i\alpha} \left[\frac{\partial^{(n)} \psi_{i\alpha}}{\partial t} + \mathbf{v}_{i\alpha}\cdot \left(\mathbf{l} - \mathbf{l}_{\alpha}^{(n)} \right) \cdot \mathbf{g}_{i\alpha} \right] \right\rangle_{\Omega_\alpha,\Omega} \\
&- \sum_{i \in \mathfrak{I}_s} \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha,\Omega} = 0 \,, \qquad (6.197)
\end{aligned}
$$

where

$$
\overset{\kappa\to\alpha}{G_0} = \sum_{i \in \mathfrak{I}_s} \overset{i\kappa\to i\alpha}{G} \qquad (6.198)
$$

and

$$
\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{i\alpha}}} \,. \qquad (6.199)
$$

Recall that in Eq. (6.197) $n = 3 - \dim \alpha$.

The consequence of this formulation is that the diffusion velocity is explicitly included in the equations as appropriate while the flux terms in the energy and entropy equations are dealt with on an entity basis. The set of exchange terms between connected sets is given by

$$
\mathfrak{X} = \{ \overset{i\kappa\to i\alpha}{M}, \overset{j\kappa\to i\alpha}{\mathbf{T}}, \overset{\kappa\to\alpha}{Q_0}, \overset{\kappa\to\alpha}{\Phi_0}, \overset{\kappa\to\alpha}{G_0} \} \quad \text{for } \alpha \in \mathfrak{I}; \kappa \in \mathfrak{I}_{c\alpha}; i,j \in \mathfrak{I}_s \,. \qquad (6.200)
$$

Note the similarity of this set with that employed when all the conservation and balance equations are species based, Eq. (6.187). The reduction in the number of exchange terms corresponds to the reduction in the number of equations. A formulation in terms of these equations will not need a closure relation for the diffusion velocity because the N species momentum equations are posed in terms of the phase velocity, $\mathbf{v}^{\overline{\alpha}}$, and $N-1$ diffusion velocities, $\mathbf{u}^{\overline{\overline{i\alpha}}}$ [2].

6.9.3 Entity-based Momentum, Energy, and Entropy

Probably the most widely used modeling framework for environmental problems, if not all flow and transport problems, involves accounting for mass transport of chemical species while considering momentum and energy transport on an entity basis. To incorporate this approach into the momentum and energy equations, there is a need to make use of an alternative collection of terms in formulating exchange processes and non-advective fluxes.

The species mass transport equation is employed as in Table 6.2. The momentum equation is re-expressed as

$$
\begin{aligned}
\mathcal{P}_{**}^{\overline{\overline{\alpha}}} = {} & \frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\right) + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}} \\
& - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{J}_s}\overset{i\kappa\to i\alpha}{M}\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} + \mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right) - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{\mathbf{T}_0} - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}}\overset{\kappa\to\alpha}{\mathbf{T}^{*}} \\
& - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{+}}\overset{\kappa\to\alpha}{\mathbf{T}^{*}} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right) = \mathbf{0} \quad \text{for } \alpha\in\mathfrak{J}\,,
\end{aligned}
\tag{6.201}
$$

where

$$
\overset{\kappa\to\alpha}{\mathbf{T}_0} = \sum_{i\in\mathfrak{J}_s}\sum_{j\in\mathfrak{J}_s}\overset{j\kappa\to i\alpha}{\mathbf{T}}\,. \tag{6.202}
$$

Equation (6.201) is obtained from Table 6.3, or Eq. (6.100), by substituting in the identities given by Eqs. (6.70), (6.94), and (6.97). Thus, it is still an entity-based equation; but the exchange terms and the gravitational term have been left in more general forms that account for species behavior.

The appropriate form of the energy equation can be developed based on Eq. (6.131) or, more directly, by rearranging Eq. (6.194). In either case, the result is

$$
\begin{aligned}
\mathcal{E}_{**}^{\overline{\overline{\alpha}}} = {} & \frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left\{E^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left[\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2} + \sum_{i\in\mathfrak{J}_s}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\right\} \\
& + \left\{E^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left[\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2} + \sum_{i\in\mathfrak{J}_s}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\right\}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}} \\
& - \sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\left(\mathbf{v}^{\overline{\alpha}} + \mathbf{u}^{\overline{\overline{i\alpha}}}\right) - \varepsilon^{\overline{\overline{\alpha}}}h_0^{\overline{\overline{\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}h^{\alpha} \\
& - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{J}_s}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}} + \frac{\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} + \mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} + \mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)}{2} + K_{Ei}^{\overline{\overline{\alpha,\kappa}}}\right] \\
& - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{Q_1} \\
& - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}}\overset{\kappa\to\alpha}{\mathbf{T}^{*}}\cdot\mathbf{v}_{\alpha}^{\overline{\kappa}} - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}}\overset{\kappa\to\alpha}{Q_1^{*}} \\
& - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{+}}\overset{\kappa\to\alpha}{\mathbf{T}^{*}}\cdot\mathbf{v}_{\kappa}^{\overline{\alpha}} - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{+}}\overset{\kappa\to\alpha}{Q_1^{*}} \\
& - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}} + \varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right) = 0\,,
\end{aligned}
\tag{6.203}
$$

where

$$\overset{\kappa\to\alpha}{Q_1} = \overset{\kappa\to\alpha}{Q_0} + \sum_{i\in\mathfrak{I}_s} \sum_{j\in\mathfrak{I}_s} \overset{j\kappa\to i\alpha}{\mathbf{T}} \cdot \mathbf{u}^{\overline{\overline{\overline{i\alpha,j\kappa}}}} . \tag{6.204}$$

The entropy balance and the body force potential equation, Eqs. (6.195) and (6.197), respectively, are not affected by having momentum conservation expressed on an entity basis. The exchange terms between entities and their connected sets are comprised of the set

$$\mathfrak{X} = \{ \overset{i\kappa\to i\alpha}{M} , \overset{\kappa\to\alpha}{\mathbf{T}_0} , \overset{\kappa\to\alpha}{Q_1} , \overset{\kappa\to\alpha}{\Phi_0} , \overset{\kappa\to\alpha}{G_0} \} \quad \text{for } \alpha \in \mathfrak{I}; \kappa \in \mathfrak{I}_{c\alpha}; i \in \mathfrak{I}_s . \tag{6.205}$$

The reduction of the size of this set due to momentum being formulated on an entity basis is accompanied by the requirement that the energy transfer term account for inter-entity mechanical effects due to diffusion.

6.10 Internal Energy Equation

In some instances, it is desirable to model the internal energy, or thermal, aspects of a problem rather than the total energy. In those cases, it is convenient to make use of an internal energy equation rather than the total energy equation. It is essential to realize that the internal energy equation is not an additional independent relation. Rather, it arises from splitting off the elements of the total energy equation that are related to thermal processes and accounting for the transfer of energy into its mechanical part. Mathematically, the fact that the internal energy equation is not an independent relation can be seen from the fact that it is derived by combining the total energy, momentum, and mass conservation equations for the purpose of eliminating the time derivative of the kinetic energy. This has the additional effect of eliminating terms in the equation related to mechanical processes. The formulation of an internal energy equation is not unique.

6.10.1 Species- and Entity-based Equations

As an example, we can form the species-based internal energy equation, $\mathcal{U}_*^{\overline{\overline{i\alpha}}}$, from the species-based conservation equations as

$$\mathcal{U}_*^{\overline{\overline{i\alpha}}} := \mathcal{E}_*^{\overline{\overline{i\alpha}}} - \mathbf{v}^{\overline{i\alpha}} \cdot \mathcal{P}_*^{\overline{\overline{i\alpha}}} + \frac{\mathbf{v}^{\overline{i\alpha}} \cdot \mathbf{v}^{\overline{i\alpha}}}{2} \mathcal{M}_*^{\overline{\overline{i\alpha}}} = 0 , \tag{6.206}$$

where the energy, momentum, and species conservation equations are taken from Table 6.2. Note that this equation is merely a sum of the total energy equation with other conservation equations that makes use of particular velocities as coefficients. Those coefficients are arbitrary in assuring that the sum of the equations is zero because each of the equations is itself zero. This particular combination of equations eliminates the material derivative of $\mathbf{v}^{\overline{i\alpha}}\cdot\mathbf{v}^{\overline{i\alpha}}$ so that the species-based internal energy equation is written in terms of a material derivative of $E^{\overline{\overline{i\alpha}}} + K_E^{\overline{\overline{i\alpha}}}$. The $K_E^{\overline{\overline{i\alpha}}}$ term accounts for subscale species motion and can be thought of as contributing to the effective internal energy.

If one works from the entity-based equations of Table 6.3, then the entity-based internal energy equation, $\mathcal{U}_*^{\overline{\overline{\alpha}}}$, is proposed to be

$$\mathcal{U}_*^{\overline{\overline{\alpha}}} := \mathcal{E}_*^{\overline{\overline{\alpha}}} - \mathbf{v}^{\overline{\alpha}}\cdot\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}} + \frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\mathcal{M}_*^{\overline{\overline{\alpha}}} = 0\,. \tag{6.207}$$

The sum of the species-based mass, momentum, and total energy equations over all species yields the respective entity-based equations. However, if one sums Eq. (6.206) over all species, the resulting collection of terms is different from those on the right side of Eq. (6.207). In fact, because $\mathbf{v}^{\overline{i\alpha}} = \mathbf{v}^{\overline{\alpha}} + \mathbf{u}^{\overline{\overline{i\alpha}}}$, it can be seen that

$$\sum_{i\in\mathfrak{I}_s} \mathcal{U}_*^{\overline{\overline{i\alpha}}} = \mathcal{U}_*^{\overline{\overline{\alpha}}} - \sum_{i\in\mathfrak{I}_s} \mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\left[\boldsymbol{\mathcal{P}}_*^{\overline{\overline{i\alpha}}} - \left(\mathbf{v}^{\overline{\alpha}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\mathcal{M}_*^{\overline{\overline{i\alpha}}}\right] = 0\,. \tag{6.208}$$

Although the forms of the equations obtained by summing a species-based internal energy equation as opposed to obtaining them from the entity-based conservation equations are different, both are equally valid. They are obtained by combining collections of terms that sum to zero, but the collections are combined differently. If one chose to formulate Eq. (6.206) using entity velocities rather than species velocities as the weighting factors, the sum of the resultant species equation over all species would be equivalent to the result obtained in Eq. (6.207).

The differences between forms lies in the fact that the breaking of the total energy equation into its internal and mechanical energy parts occurs at a different point in the two approaches. The cleavage point is immaterial as long as the transfer of energy between the elements of the equation is accounted for properly. Because the total energy equation accounts for all the energy in the system, it is unique; summation of the unique species-based equations must yield the unique entity-based equation. However, internal energy is only part of the system energy. The use of arbitrary velocity coefficients along with momentum and mass equations to attempt to formulate an equation called the internal energy equation provides different forms depending on the way terms are combined.

6.10.2 Mixed Formulation with Species Conservation

When working with mixed forms of macroscale equations, the selection of appropriate coefficients for formulation of an internal energy equation is also subjective. It is difficult to decide whether to make use of species or entity based velocities in combining terms. For later use, we will define the internal energy equation for the case when the momentum and energy equations are entity-based but the mass conservation equations are species-based as

$$\mathcal{U}_{**}^{\overline{\overline{\alpha}}} := \mathcal{E}_{**}^{\overline{\overline{\alpha}}} - \mathbf{v}^{\overline{\alpha}}\cdot\mathcal{P}_{**}^{\overline{\overline{\alpha}}} + \sum_{i\in\mathfrak{J}_s} \frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\mathcal{M}_{**}^{\overline{\overline{i\alpha}}} = 0\,, \tag{6.209}$$

where $\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$ is taken from Eq. (6.203), $\mathcal{P}_{**}^{\overline{\overline{\alpha}}}$ is provided in Eq. (6.201), and $\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$ is given by Eq. (6.74).

Substitution of the specific forms into Eq. (6.209) and rearrangement of terms yields

$$\begin{aligned}
\mathcal{U}_{**}^{\overline{\overline{\alpha}}} :=& \frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left[E^{\overline{\overline{\alpha}}} + \sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right] \\
&+ \left[E^{\overline{\overline{\alpha}}} + \sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}} \\
&- \sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}h_0^{\overline{\overline{\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}h^{\alpha} \\
&- \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\ \sum_{i\in\mathfrak{J}_s} \overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}} + \frac{\left(\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}} + \mathbf{u}_i^{\overline{\overline{\overline{\alpha,\kappa}}}} - \mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}} + \mathbf{u}_i^{\overline{\overline{\overline{\alpha,\kappa}}}} - \mathbf{v}^{\overline{\alpha}}\right)}{2} + K_{Ei}^{\overline{\overline{\overline{\alpha,\kappa}}}}\right] \\
&- \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{\alpha}}\right) - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}} \overset{\kappa\to\alpha}{Q_1} \\
&- \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\ \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}} \overset{\kappa\to\alpha}{\mathbf{T}^*}\cdot\left(\mathbf{v}_{\alpha}^{\overline{\kappa}} - \mathbf{v}^{\overline{\alpha}}\right) - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}}\ \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}} \overset{\kappa\to\alpha}{Q_1^*} \\
&- \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}}\ \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{+}} \overset{\kappa\to\alpha}{\mathbf{T}^*}\cdot\left(\mathbf{v}_{\kappa}^{\overline{\alpha}} - \mathbf{v}^{\overline{\alpha}}\right) - \frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}}\ \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{+}} \overset{\kappa\to\alpha}{Q_1^*} \\
&- \varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}{:}\mathbf{d}^{\overline{\overline{\alpha}}} - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right) = 0\,.
\end{aligned} \tag{6.210}$$

This equation can be used as an alternative to the total energy equation when one wishes to focus on the internal energy aspects of a problem. Either equation, however, is satisfactory because one is obtained from the other in conjunction with mass and momentum conservation equations.

6.11 Summary

In this chapter, we have detailed the approach needed to upscale equations from the microscale to the macroscale, as depicted in Fig. 6.1. Specifically, in this chapter we have provided forms of the averaging theorems useful for modeling porous medium flow based on the general derivations in Appendix B. The theorems are listed in Table 6.1 for phases, interfaces, common curves, and common points. The theorems for phases were applied to the microscale phase equations to obtain macroscale conservation and balance equations for species in a phase and for phases as a whole. These results are collected in Tables 6.2 and 6.3. Although one could proceed by averaging the appropriate microscale equations for lower dimensional entities using the corresponding averaging theorems, we adopted a streamlined procedure. Based on understanding of the macroscale conceptualization of a system, we argued that the general macroscale equations should be identical regardless of the entity type considered. Thus, the result of deriving macroscale equations from their microscale precursors using the appropriate averaging theorems can be obtained without doing the detailed work. The equations are provided in Tables 6.2 and 6.3. The only adjustments required for different entities are in identifying the connected sets. We chose not to allow concentrated forces at common points.

Rather than leaving the averaged equations in terms of averaging operators, the equations were handled with the goal of assuring consistency of the definitions of variables across equations. Thus, although some variables are defined as intrinsic averages over the entity and others are density weighted averages, a good number of variables are defined in a unique manner. Definitions of the uniquely defined variables are provided in every instance, and the definitions are retained for all equations in which the variable appears. This is necessary to achieve the goal of producing the fewest possible number of physically reasonable macroscale variables so that the closure problem can be minimized. Thus, averages of products are expressed as products of averages with additional deviation terms; other techniques are used to break products in a way that leads to consistent formulations. The deviation terms, which account for microscale processes not explicitly modeled at the macroscale, are retained within the definitions of macroscale variables.

Although the macroscale conservation equations are of the same form regardless of the entity being considered, the equations become different through application of a closure procedure. This closure procedure will be seen to be similar to that employed in Chap. 5 for a single fluid phase. Thus, closure expressions will be developed for quantities such as the non-advective energy and momentum diffusion within an entity. Additionally, the terms expressing the exchanges of properties between entities have to be modeled. The expressions are obtained in TCAT using the full path depicted in Fig. 1.3, not just the parts of that figure highlighted in this chapter and in Fig. 6.1.

Although we now have macroscale conservation and balance equations, the two figures cited indicate that the averaging theorems must also be applied to microscale thermodynamic equations and equilibrium conditions to complete the transfer of all microscale perspectives to the macroscale. This will be the focus of the next chapter as we build all the elements needed to obtain closed dynamic equations for macroscale processes. The use of averaging theorems to obtain evolution equations is considered subsequently.

Exercises

6.1. Show that the definition of $\mathbf{t}^{\overline{\overline{\alpha}}}$ given in Eq. (6.95) is the same definition that one would obtain if momentum Eq. (6.92) is obtained directly from averaging Eq. (2.27).

6.2. Show that the definition of $\overset{\kappa\to\alpha}{\mathbf{T}}$ given in Eq. (6.97) is the same definition that one would obtain if momentum Eq. (6.92) is obtained directly from averaging Eq. (2.27).

6.3. Show that the definition of $\mathbf{q}^{\overline{\overline{\alpha}}}$ given in Eq. (6.123) is the same definition that one would obtain if energy Eq. (6.118) is obtained directly from averaging Eq. (2.32).

6.4. Show that the definition of $\mathbf{t}^{\overline{\overline{i\alpha}}\mathrm{T}}$ given in Eq. (6.79) obtained by averaging over a phase entity is identical to that obtained by averaging the species momentum equation for a common curve.

6.5. Show that the expressions for the energy exchange term, $\overset{\kappa\to\alpha}{Q}$, given in Table 6.3 and Eq. (6.129), are equivalent.

6.6. Derive the entity-based macroscale momentum equation for a common curve from the microscale equations using the averaging theorems in the [1,(3,0),0] family.

6.7. Sometimes it is convenient to formulate the energy equation making use of the body force potential instead of the body force per unit entity measure. Assume the body force potential is independent of time and acts equally on all species (e.g., this is the way gravity behaves).

- **a.** Combine $\mathcal{G}^{\overline{\overline{i\alpha}}}$ with $\mathcal{E}^{\overline{\overline{i\alpha}}}$ to obtain this modified species-based energy equation.
- **b.** Combine $\mathcal{G}^{\overline{\overline{\alpha}}}$ with $\mathcal{E}^{\overline{\overline{\alpha}}}$ to obtain this modified entity-based energy equation.
- **c.** Show that your answer to part b is consistent with the result obtained by summing your answer to part a over all species.

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Chapter 7
Macroscale Thermodynamics

7.1 Overview

A unique feature of the TCAT approach is the treatment of thermodynamics at the macroscale. Alternative averaging theories either ignore thermodynamics completely or introduce thermodynamics directly at the macroscale using the rational thermodynamics approach. Both of these approaches sometimes violate known microscale thermodynamic principles. In any event, without interscale consistency of a thermodynamic formulation, it is not possible to relate experimental measurements and variables across scales. The physical meaning of quantities such as temperature, pressure, and entropy that are designated symbolically at the macroscale can be obscured. By averaging microscale thermodynamic theory to the macroscale, TCAT ensures consistency and provides unambiguous opportunities for obtaining meaningful closure relations, cross-scale simulations, and support for the macroscale theories from small scale simulations.

In the TCAT approach, any consistent microscale thermodynamic theory can serve as the basis for the macroscale thermodynamic formalism. Some reasonable candidates are mentioned briefly in Sect. 3.12. However, we choose to use Classical Irreversible Thermodynamics (CIT), described in Sect. 3.11, because it is relatively simple and has been used successfully in describing the behavior of many systems at the microscale. Within the TCAT framework, as depicted in Fig. 7.1, the microscale thermodynamic relations and equilibrium expressions are converted to a larger scale of interest using the averaging conventions and theorems described in the last chapter. This approach yields a rigorous thermodynamic basis for macroscale thermodynamic variables that are defined precisely in terms of microscale precursors. Thus, the procedure for change in scale of thermodynamic expressions mimics that employed for changing the scale of conservation and balance equations. The fact that TCAT uses averaging of thermodynamic expressions will be shown to be a significant point of departure from other averaging theories that resolves some long standing, and recently introduced, problems that exist with alternative approaches.

W. G. Gray and C. T. Miller, *Introduction to the Thermodynamically Constrained Averaging Theory for Porous Medium Systems,* Advances in Geophysical and Environmental Mechanics and Mathematics, DOI: 10.1007/978-3-319-04010-3_7,

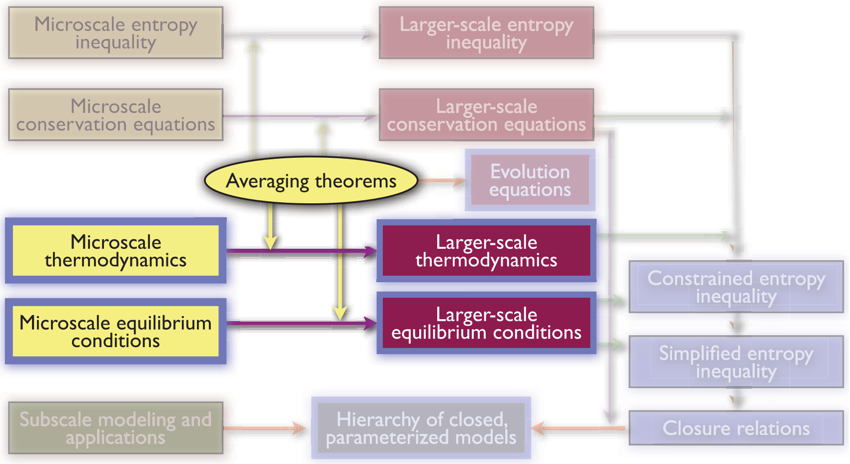

Fig. 7.1 TCAT elements of interest in Chap. 7 (after [2])

In the sections of this chapter, three main topics are considered. First, CIT thermodynamic expressions are averaged from the microscale to the macroscale and the results are discussed. Specific macroscale relations of interest include the Euler forms, the differential expressions, and the Gibbs-Duhem equations for species and for entities. Second, dynamic equations are derived that relate the rates of change of macroscale thermodynamic variables. These relations are obtained both for species and for entities in forms that are particularly useful for constraining the macroscale entropy inequality. Third, the microscale equilibrium conditions are averaged to the macroscale. These conditions provide a basis for the postulation of near-equilibrium closure relations in the context of the constrained entropy inequality.

7.2 Macroscale Euler Equations

The macroscale Euler equations are derived by averaging the microscale forms. The main issue that arises in performing this procedure is the need to break products so that macroscale variables can be defined appropriately. We will provide some explicit examples of the averaging that occurs and tabulate the results.

7.2.1 Fluid Phase

Euler equations for a fluid phase may be obtained on a species basis or for the entity as a whole. In both cases, the starting point is the corresponding microscale

Table 7.1 Macroscale Euler equations for phases, interfaces, and common curves. Equation numbers refer to microscale precursors

Entity	Basis	Euler Equation	Eq.
Phase	Species $i \in \mathfrak{J}_s$	$E^{\overline{\overline{i\alpha}}} - \theta^{\overline{\overline{i\alpha}}}\eta^{\overline{\overline{i\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} p^\alpha X^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha \omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}} = 0$	(3.169)
$\alpha \in \mathfrak{J}_\mathrm{f}$	Entity	$E^{\overline{\overline{\alpha}}} - \theta^{\overline{\overline{\alpha}}}\eta^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} p^\alpha - \sum\limits_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha \omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}} = 0$	(3.156)
Solid	Species $i \in \mathfrak{J}_s$	$E^{\overline{\overline{is}}} - \theta^{\overline{\overline{is}}}\eta^{\overline{\overline{is}}} - \varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}{:}\dfrac{\mathbf{X}^{\overline{\overline{is}}}\cdot\mathbf{C}^s}{j^s} - \varepsilon^{\overline{\overline{s}}}\rho^s \omega^{i\overline{s}}\mu^{\overline{is}} = 0$	(3.182)
	Entity	$E^{\overline{\overline{s}}} - \theta^{\overline{\overline{s}}}\eta^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}{:}\dfrac{\mathbf{C}^s}{j^s} - \sum\limits_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{s}}}\rho^s \omega^{i\overline{s}}\mu^{\overline{is}} = 0$	(3.159)
Interface	Species $i \in \mathfrak{J}_s$	$E^{\overline{\overline{i\alpha}}} - \theta^{\overline{\overline{i\alpha}}}\eta^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}\gamma^\alpha X^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha \omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}} = 0$	(3.189)
$\alpha \in \mathfrak{J}_\mathrm{I}$	Entity	$E^{\overline{\overline{\alpha}}} - \theta^{\overline{\overline{\alpha}}}\eta^{\overline{\overline{\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}\gamma^\alpha - \sum\limits_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha \omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}} = 0$	(3.161)
Curve	Species $i \in \mathfrak{J}_s$	$E^{\overline{\overline{i\alpha}}} - \theta^{\overline{\overline{i\alpha}}}\eta^{\overline{\overline{i\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\gamma^\alpha X^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha \omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}} = 0$	(3.193)
$\alpha \in \mathfrak{J}_\mathrm{C}$	Entity	$E^{\overline{\overline{\alpha}}} - \theta^{\overline{\overline{\alpha}}}\eta^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\gamma^\alpha - \sum\limits_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha \omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}} = 0$	(3.163)

Euler form. The species-based Euler equation for a fluid phase, rearranged from Eq. (3.169), is

$$E_{i\alpha} - \theta_\alpha \eta_{i\alpha} + p_\alpha X_{i\alpha} - \rho_\alpha \omega_{i\alpha}\mu_{i\alpha} = 0 \quad \text{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J}_\mathrm{f} \, . \tag{7.1}$$

Application of the averaging operator $\langle \cdot \rangle_{\Omega_\alpha,\Omega}$ to this equation gives

$$\langle E_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \langle \theta_\alpha \eta_{i\alpha}\rangle_{\Omega_\alpha,\Omega} + \langle p_\alpha X_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \langle \rho_\alpha \omega_{i\alpha}\mu_{i\alpha}\rangle_{\Omega_\alpha,\Omega} = 0 \, . \tag{7.2}$$

The need now is to break the averages of products to define products of macroscale properties. In performing this operation, it is essential to keep in mind that macroscale definitions for volume fraction (unique average $\varepsilon^{\overline{\overline{\alpha}}}$ defined in Eq. (6.9)), density (intrinsic average ρ^α), mass fraction (density weighted average $\omega^{i\overline{\alpha}}$), energy density (unique average $E^{\overline{\overline{i\alpha}}}$ defined in Eq. (6.103)), and entropy density (unique average $\eta^{\overline{\overline{i\alpha}}}$ defined in Eq. (6.135)) have already been provided in the last chapter. These definitions must be honored.

The fact that macroscale entropy density has already been defined suggests that the second term on the left side of Eq. (7.2) be expressed as

$$\theta^{\overline{\overline{i\alpha}}}\eta^{\overline{\overline{i\alpha}}} = \langle \theta_\alpha \eta_{i\alpha}\rangle_{\Omega_\alpha,\Omega} \, . \tag{7.3}$$

We make use of the unique definition of entropy density, as provided in Eq. (6.135),

$$\eta^{\overline{\overline{i\alpha}}} = \langle \eta_{i\alpha}\rangle_{\Omega_\alpha,\Omega} \, , \tag{7.4}$$

and define an entropy weighted temperature, $\theta^{\overline{\overline{i\alpha}}}$, as

$$\theta^{\overline{\overline{i\alpha}}} = \langle \theta_\alpha \rangle_{\Omega_\alpha,\Omega_\alpha,\eta_{i\alpha}} \, . \tag{7.5}$$

It is interesting to note that although all species will have the same temperature, θ_α, at a microscale point, their macroscale temperatures need not be equal because the weighting function for averaging is different for each species. If the microscale temperature is constant within an averaging region, all macroscale species temperatures will be equal. However, when a temperature gradient exists, the different weighting functions for the different species could lead to different macroscale temperatures. Whether or not such a difference needs to be considered in a model depends on length scale and the magnitude of the error introduced by neglecting this effect in comparison to other sources of error.

Because macroscale analogs of pressure and $X_{i\alpha}$ have not been encountered previously, it seems reasonable that we could define a macroscale pressure as an $X_{i\alpha}$-weighted average or define $X^{\overline{\overline{i\alpha}}}$ as a pressure-weighted average. We choose the latter approach and define

$$\varepsilon^{\overline{\overline{\alpha}}} p^\alpha X^{\overline{\overline{i\alpha}}} = \langle p_\alpha X_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{f} \, , \tag{7.6}$$

where

$$X^{\overline{\overline{i\alpha}}} = \langle X_{i\alpha} \rangle_{\Omega_\alpha,\Omega_\alpha,p_\alpha} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{f} \, . \tag{7.7}$$

This definition preserves the condition that the sum of $X_{i\alpha}$ is equal to 1 in the macroscopic form

$$1 = \sum_{i \in \mathfrak{I}_s} X^{\overline{\overline{i\alpha}}} \, . \tag{7.8}$$

The last term in Eq. (7.2) is expressed in terms of a density-weighted chemical potential such that

$$\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mu^{\overline{i\alpha}} = \langle \rho_\alpha \omega_{i\alpha} \mu_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{f} \, . \tag{7.9}$$

Retaining the definition of $E^{\overline{\overline{i\alpha}}}$ given in Eq. (6.103),

$$E^{\overline{\overline{i\alpha}}} = \langle E_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \, , \tag{7.10}$$

we can write Eq. (7.2) in terms of macroscale variables,

$$E^{\overline{\overline{i\alpha}}} - \theta^{\overline{\overline{i\alpha}}} \eta^{\overline{\overline{i\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} p^\alpha X^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \mu^{\overline{i\alpha}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{f} \, . \tag{7.11}$$

This equation has been entered as the first line of Table 7.1.

To obtain the Euler equation based on the fluid phase entity as a whole, two approaches are possible. One method is to begin with Eq. (3.156) and average it. Note that Eq. (3.156) is equal to the sum of Eq. (3.169) over all species. This microscale equality must be retained at the macroscale. Thus, the sum of Eq. (7.11) over all species must be consistent with the entity-based form obtained directly by averaging with

$$\sum_{i\in\mathcal{J}_s}\left(E^{\overline{\overline{i\alpha}}}-\theta^{\overline{\overline{i\alpha}}}\eta^{\overline{\overline{i\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}X^{\overline{\overline{i\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}}\right)=0\quad\text{for }\alpha\in\mathcal{J}_{\mathrm{f}}\,. \tag{7.12}$$

Making use of Eq. (6.119), which defines $E^{\overline{\overline{\alpha}}}$ as the sum of $E^{\overline{\overline{i\alpha}}}$ over all species, Eq. (6.145), which defines $\eta^{\overline{\overline{\alpha}}}$ as the sum of $\eta^{\overline{\overline{i\alpha}}}$ over all species, and of Eq. (7.8), we obtain

$$E^{\overline{\overline{\alpha}}}-\theta^{\overline{\overline{\alpha}}}\eta^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}-\sum_{i\in\mathcal{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}}=0\quad\text{for }\alpha\in\mathcal{J}_{\mathrm{f}}\,. \tag{7.13}$$

We have made use of the fact that

$$\sum_{i\in\mathcal{J}_s}\theta^{\overline{\overline{i\alpha}}}\eta^{\overline{\overline{i\alpha}}}=\sum_{i\in\mathcal{J}_s}\langle\theta_{\alpha}\eta_{i\alpha}\rangle_{\Omega_{\alpha},\Omega}=\left\langle\theta_{\alpha}\sum_{i\in\mathcal{J}_s}\eta_{i\alpha}\right\rangle_{\Omega_{\alpha},\Omega}=\langle\theta_{\alpha}\eta_{\alpha}\rangle_{\Omega_{\alpha},\Omega}\,, \tag{7.14}$$

so that

$$\theta^{\overline{\overline{\alpha}}}=\langle\theta_{\alpha}\rangle_{\Omega_{\alpha},\Omega_{\alpha},\eta_{\alpha}}\,. \tag{7.15}$$

Equation (7.13) is entered into Table 7.1. It is straightforward to show that this result is also obtained by averaging Eq. (3.156).

7.2.2 Solid Phase

The derivation of the solid phase Euler equations follows the same path as that for the fluid phases. The results of the derivation are given in Table 7.1. The main issue in these expressions is the proper definition of the unique averages that arise. In particular, for the species-based equation, the term involving the stress is rather complex. We note that the stresses that appear in this relation are defined relative to the undeformed coordinate system. Thus we can write

$$\left\langle\sigma_s{:}\frac{\mathbf{X}_{is}\cdot\mathbf{C}_s}{j_s}\right\rangle_{\Omega_s,\Omega}=\langle\sigma_s{:}(\mathbf{X}_{is}\cdot\mathbf{C}_s)\rangle_{\Omega_{s0},\Omega}\,, \tag{7.16}$$

where the jacobian has been used to change the region of integration from the deformed region occupied by the solid to the initial domain, Ω_{s0}. Then we define

$$\mathbf{C}^{s}=\langle\mathbf{C}_s\rangle_{\Omega_{s0},\Omega_{s0}}\,, \tag{7.17}$$

where the intrinsic average notation is used because the average is calculated and normalized over the domain where the function is defined[1]. We then define

$$\sigma^{\overline{\overline{s}}}{:}\mathbf{C}^{s} = \langle \sigma_s{:}\mathbf{C}_s \rangle_{\Omega_{s0},\Omega_{s0}} \tag{7.18}$$

and

$$\sigma^{\overline{\overline{s}}}{:}\left(\mathbf{X}^{\overline{\overline{is}}}\cdot\mathbf{C}^{s}\right) = \langle \sigma_s{:}\left(\mathbf{X}_{is}\cdot\mathbf{C}_s\right) \rangle_{\Omega_{s0},\Omega_{s0}} \,. \tag{7.19}$$

These last two relations provide the definitions for the unique averages $\sigma^{\overline{\overline{s}}}$ and $\mathbf{X}^{\overline{\overline{is}}}$. Equation (7.19) can revert to the average over Ω_s that we seek. If we change the normalizing volume to Ω, then the equation becomes

$$\varepsilon^{\overline{\overline{s0}}}\sigma^{\overline{\overline{s}}}{:}\left(\mathbf{X}^{\overline{\overline{is}}}\cdot\mathbf{C}^{s}\right) = \langle \sigma_s{:}\left(\mathbf{X}_{is}\cdot\mathbf{C}_s\right) \rangle_{\Omega_{s0},\Omega} \,, \tag{7.20}$$

where

$$\varepsilon^{\overline{\overline{s0}}} = \langle 1 \rangle_{\Omega_{s0},\Omega} \,. \tag{7.21}$$

However, $\varepsilon^{\overline{\overline{s}}} = j^{s}\varepsilon^{\overline{\overline{s0}}}$. Therefore, we can substitute this identity into Eq. (7.20) and change the domain of integration on the right side to Ω_s by reintroducing the microscale jacobian so that we obtain

$$\varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}{:}\frac{\mathbf{X}^{\overline{\overline{is}}}\cdot\mathbf{C}^{s}}{j^{s}} = \left\langle \sigma_s{:}\frac{\mathbf{X}_{is}\cdot\mathbf{C}_s}{j_s} \right\rangle_{\Omega_s,\Omega} \,. \tag{7.22}$$

This is the expression that appears in Table 7.1.

For the entity-based solid thermodynamics, the identity employed is

$$\varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}{:}\frac{\mathbf{C}^{s}}{j^{s}} = \left\langle \sigma_s{:}\frac{\mathbf{C}_s}{j_s} \right\rangle_{\Omega_s,\Omega} \,, \tag{7.23}$$

which follows the derivation from Eq. (7.18) to Eq. (7.22). Summation of Eq. (7.22) over all species provides the desirable condition of consistency with Eq. (7.23) when

$$\mathbf{I} = \sum_{i\in\mathfrak{I}_s} \mathbf{X}_{is} = \sum_{i\in\mathfrak{I}_s} \mathbf{X}^{\overline{\overline{is}}} \,. \tag{7.24}$$

7.2.3 Interface and Common Curve

The derivation of the Euler equation for an interface or common curve is almost identical to that employed for a fluid phase. The only differences are the replacement

---

[1] One could argue correctly that the macroscopic Green's tensor should be denoted as $\mathbf{C}^{s0}$ for perfectly consistent notation. However, the addition of the superscript "0" is unnecessarily cumbersome and is thus not used.

of pressure with interfacial tension in the case of an interface and with lineal tension for a common curve. Then the definition of the variable $X^{\overline{\overline{i\alpha}}}$, as provided in Eq. (7.7), is modified slightly such that

$$X^{\overline{\overline{i\alpha}}} = \langle X_{i\alpha} \rangle_{\Omega_\alpha,\Omega_\alpha,\gamma_\alpha} \quad \text{for } i \in \mathfrak{J}_s; \alpha \in \mathfrak{J}_\mathrm{I} \cup \mathfrak{J}_\mathrm{C} \,. \tag{7.25}$$

The Euler equations for interfaces and common curves are listed in Table 7.1.

7.3 Macroscale Energy Differentials

Although the macroscale Euler equations are cosmetically similar to their microscale precursors, with the main notational difference being the presence of superscripts rather than subscripts, these equations are substantively different. At the microscale, the energy density is a function of mass and entropy densities, as given in Eq. (3.197) for a fluid phase under the CIT formalism. However, it has been noted that in inhomogeneous systems, a larger scale energy is no longer a function only of these same variables at a larger scale [3]. The importance of this observation is typically overlooked when one formulates the thermodynamics directly at the larger scale, effectively assuming that a local equilibrium assumption applies at the larger scale. This fact can be demonstrated by examining the differentials of macroscale energy in Table 7.1 for a fluid.

The differential of the energy expression for species i in a fluid phase α is obtained from Eq. (7.11), the first line in Table 7.1. as

$$\begin{aligned} &\mathrm{d}E^{\overline{\overline{i\alpha}}} - \theta^{\overline{\overline{i\alpha}}}\,\mathrm{d}\eta^{\overline{\overline{i\alpha}}} + p^\alpha\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}} X^{\overline{\overline{i\alpha}}}\right) - \mu^{\overline{i\alpha}}\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}}\right) \\ &\quad - \eta^{\overline{\overline{i\alpha}}}\,\mathrm{d}\theta^{\overline{\overline{i\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} X^{\overline{\overline{i\alpha}}}\,\mathrm{d}p^\alpha - \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}}\,\mathrm{d}\mu^{\overline{i\alpha}} = 0 \quad \text{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J}_\mathrm{f} \,. \end{aligned} \tag{7.26}$$

The last three terms on the left side of this equation may be rewritten in terms of the averaging operator so that Eq. (7.26) becomes

$$\begin{aligned} &\mathrm{d}E^{\overline{\overline{i\alpha}}} - \theta^{\overline{\overline{i\alpha}}}\,\mathrm{d}\eta^{\overline{\overline{i\alpha}}} + p^\alpha\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}} X^{\overline{\overline{i\alpha}}}\right) - \mu^{\overline{i\alpha}}\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}}\right) \\ &\quad - \left\langle \eta_{i\alpha}\,\mathrm{d}\theta^{\overline{\overline{i\alpha}}} \right\rangle_{\Omega_\alpha,\Omega} + \langle X_{i\alpha}\,\mathrm{d}p^\alpha \rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha \omega_{i\alpha}\,\mathrm{d}\mu^{\overline{i\alpha}} \right\rangle_{\Omega_\alpha,\Omega} = 0 \,. \end{aligned} \tag{7.27}$$

The microscale Gibbs-Duhem equation provided as Eq. (3.175) can be averaged to obtain

$$\begin{aligned} &\langle \eta_{i\alpha}\mathrm{d}\theta_\alpha \rangle_{\Omega_\alpha,\Omega} - \langle X_{i\alpha}\mathrm{d}p_\alpha \rangle_{\Omega_\alpha,\Omega} + \langle \rho_\alpha \omega_{i\alpha}\mathrm{d}\mu_{i\alpha} \rangle_{\Omega_\alpha,\Omega} \\ &\quad - \left\langle \rho_\alpha \omega_{i\alpha} \left(\mathrm{d}\mu_{i\alpha}\right)\big|_{p_\alpha,\theta_\alpha} \right\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J}_\mathrm{f} \,. \end{aligned} \tag{7.28}$$

Addition of this equation to Eq. (7.27) then gives

$$
\begin{aligned}
&\mathrm{d}E^{\overline{\overline{i\alpha}}} - \theta^{\overline{\overline{i\alpha}}}\,\mathrm{d}\eta^{\overline{\overline{i\alpha}}} + p^{\alpha}\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}}X^{\overline{\overline{i\alpha}}}\right) - \mu^{\overline{i\alpha}}\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\right)\\
&\quad - \left\langle \rho_{\alpha}\omega_{i\alpha}\left(\mathrm{d}\mu_{i\alpha}\right)\big|_{p_{\alpha},\theta_{\alpha}}\right\rangle_{\Omega_{\alpha},\Omega} + \left\langle \eta_{i\alpha}\,\mathrm{d}\left(\theta_{\alpha} - \theta^{\overline{\overline{i\alpha}}}\right)\right\rangle_{\Omega_{\alpha},\Omega}\\
&\quad - \left\langle X_{i\alpha}\,\mathrm{d}\left(p_{\alpha} - p^{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega} + \left\langle \rho_{\alpha}\omega_{i\alpha}\,\mathrm{d}\left(\mu_{i\alpha} - \mu^{\overline{i\alpha}}\right)\right\rangle_{\Omega_{\alpha},\Omega} = 0\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{f}}\,. \qquad (7.29)
\end{aligned}
$$

The last three terms on the left side involve averages of differentials of differences between microscale and macroscale quantities. For the case of a system that is essentially homogeneous within each averaging volume, these averages will be zero so that the terms drop out. In that instance, the equation for the differential of energy is the same as the microscale expression in Eq. (3.173). This confirms the observation that when a system is not homogeneous, the dependence of microscale energy on independent variables will be different from the dependence of macroscale energy on independent variables. The TCAT approach includes this additional dependence as a natural consequence of averaging the thermodynamic expression. When these terms do not appear, there is an inherent assumption that local equilibrium applies at the macroscale.

The species-based Gibbs-Duhem equation may be obtained by subtracting Eq. (7.26) from Eq. (7.29) so that

$$
\begin{aligned}
&\eta^{\overline{\overline{i\alpha}}}\,\mathrm{d}\theta^{\overline{\overline{i\alpha}}} - \varepsilon^{\overline{\overline{\alpha}}}X^{\overline{\overline{i\alpha}}}\,\mathrm{d}p^{\alpha} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\,\mathrm{d}\mu^{\overline{i\alpha}} - \left\langle \rho_{\alpha}\omega_{i\alpha}\left(\mathrm{d}\mu_{i\alpha}\right)\big|_{p_{\alpha},\theta_{\alpha}}\right\rangle_{\Omega_{\alpha},\Omega}\\
&+ \left\langle \eta_{i\alpha}\,\mathrm{d}\left(\theta_{\alpha} - \theta^{\overline{\overline{i\alpha}}}\right)\right\rangle_{\Omega_{\alpha},\Omega} - \left\langle X_{i\alpha}\,\mathrm{d}\left(p_{\alpha} - p^{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\\
&+ \left\langle \rho_{\alpha}\omega_{i\alpha}\,\mathrm{d}\left(\mu_{i\alpha} - \mu^{\overline{i\alpha}}\right)\right\rangle_{\Omega_{\alpha},\Omega} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{f}}\,. \qquad (7.30)
\end{aligned}
$$

This equation differs from the microscale Gibbs-Duhem form in the presence of the deviation terms that account for situations where the local equilibrium assumption does not apply at the macroscale.

For the fluid phase entity, the differential of energy may alternatively be obtained by summing Eq. (7.26) over all species $i \in \mathfrak{I}_s$ or by taking the differential of the Euler expression for a fluid phase in Table 7.1. In either case, the result is

$$
\begin{aligned}
&\mathrm{d}E^{\overline{\overline{\alpha}}} - \theta^{\overline{\overline{\alpha}}}\,\mathrm{d}\eta^{\overline{\overline{\alpha}}} + p^{\alpha}\,\mathrm{d}\varepsilon^{\overline{\overline{\alpha}}} - \sum_{i\in\mathfrak{I}_s} \mu^{\overline{i\alpha}}\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\right)\\
&\quad - \eta^{\overline{\overline{\alpha}}}\,\mathrm{d}\theta^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\,\mathrm{d}p^{\alpha} - \sum_{i\in\mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\,\mathrm{d}\mu^{\overline{i\alpha}} = 0 \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}}\,. \qquad (7.31)
\end{aligned}
$$

Summation of Eq. (7.27) over all species i provides the differential of the energy as

$$
\begin{aligned}
&\mathrm{d}E^{\overline{\overline{\alpha}}} - \theta^{\overline{\overline{\alpha}}}\,\mathrm{d}\eta^{\overline{\overline{\alpha}}} + p^{\alpha}\,\mathrm{d}\varepsilon^{\overline{\overline{\alpha}}} - \sum_{i\in\mathfrak{I}_s} \mu^{\overline{i\alpha}}\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\right)\\
&\quad + \left\langle \eta_{\alpha}\,\mathrm{d}\left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}}\right)\right\rangle_{\Omega_{\alpha},\Omega} - \left\langle \mathrm{d}\left(p_{\alpha} - p^{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}
\end{aligned}
$$

$$+\sum_{i\in\mathfrak{I}_s}\left\langle \rho_\alpha \omega_{i\alpha}\,\mathrm{d}\left(\mu_{i\alpha}-\mu^{\overline{i\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega}=0 \quad \text{for } \alpha\in\mathfrak{I}_\mathrm{f}\,. \tag{7.32}$$

The Gibbs-Duhem equation obtained as a sum of Eq. (7.30) over all species is

$$\eta^{\overline{\overline{\alpha}}}\,\mathrm{d}\theta^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\,\mathrm{d}p^\alpha+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\,\mathrm{d}\mu^{\overline{i\alpha}}+\left\langle \eta_\alpha\,\mathrm{d}\left(\theta_\alpha-\theta^{\overline{\overline{\alpha}}}\right)\right\rangle_{\Omega_\alpha,\Omega}$$
$$-\left\langle \mathrm{d}\left(p_\alpha-p^\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}+\sum_{i\in\mathfrak{I}_s}\left\langle \rho_\alpha\omega_{i\alpha}\,\mathrm{d}\left(\mu_{i\alpha}-\mu^{\overline{i\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega}=0 \quad \text{for } \alpha\in\mathfrak{I}_\mathrm{f}\,. \tag{7.33}$$

The deviation terms in the last two equations will drop out for a system that is homogeneous at the macroscale.

The analysis in this section has been in the context of a fluid phase for the purpose of showing that terms accounting for macroscale inhomogeneity arise in the expression for the differential of macroscale energy and in the Gibbs-Duhem equation. Virtually identical analyses provide the same conclusion if considering a solid phase, an interface, or a common curve. If the extra terms are overlooked, as happens when one hypothesizes the thermodynamic formalism directly at the macroscale, the meaning of the surviving quantities in the equations can be unclear. For example, suppose that one omits the terms involving deviations from Eq. (7.32) such that the differential of energy is described as

$$\mathrm{d}E^{\overline{\overline{\alpha}}}-\theta^{\overline{\overline{\alpha}}}\,\mathrm{d}\eta^{\overline{\overline{\alpha}}}+p^\alpha\,\mathrm{d}\varepsilon^{\overline{\overline{\alpha}}}-\sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\alpha}}\,\mathrm{d}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\right)=0 \quad \text{for } \alpha\in\mathfrak{I}_\mathrm{f}\,. \tag{7.34}$$

For this equality to be satisfied when the deviation terms are important, the definitions of the macroscale variables must be something other than their explicit definitions obtained from averaging. Thus, although one can proceed with this simplified equation and claim that p^α is a macroscale pressure, the actual meaning of the quantity designated as p^α, as well as other macroscale variables, is obscure. Supporting a developed model experimentally or across scales when the meaning of the variables that appear is unclear is not possible.

With this background on the importance of handling differentials of macroscale thermodynamic relations rigorously, we now turn to the derivation of dynamic expressions involving material time derivatives of the Euler equations. These equations are important elements of the full theory because they establish the relations between changes in entropy density in the entropy balance equation and changes in energy and mass densities that appear in the conservation equations.

7.4 Fluid Energy Dynamics

The purpose of this section is to derive a form of the material derivative of the Euler equation for chemical species in a fluid and for the fluid entity. The equations developed are of utility in constraining the macroscale entropy inequality in the same way that the microscopic expression for $\mathcal{T}_{*\alpha}$ with $\alpha = w \in \mathcal{I}_\mathrm{f}$ from Table 3.1 was introduced in Sect. 5.4.1 as a constraint on the microscale entropy inequality. We will also derive equations for the material derivative of the body force potential analogous to the microscale expressions given in Eqs. (2.45) and (2.48) for a species and an entity, respectively. Although the material derivative of an Euler equation is simple to state, and indeed will be stated here, this first expression is not in a form that is most useful for porous medium analysis. We will therefore manipulate the equation further to its most useful form for application. These manipulations anticipate subsequent needs. The full derivation could be postponed until implementation with the entropy inequality for a system of interest. However, it is convenient to complete the derivation in this chapter and make use of the result.

7.4.1 Fluid Species Energy

The Euler equation for the species energy in a fluid phase is given in Eq. (7.11) and also Table 7.1. The material derivative of this equation taken with velocity $\mathbf{v}^{\overline{i\alpha}}$ is

$$\frac{\mathrm{D}^{\overline{i\alpha}}E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{i\alpha}}\eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} - \eta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{i\alpha}}\theta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t}$$
$$+ \frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}X^{\overline{\overline{i\alpha}}})}{\mathrm{D}t} - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}\mu^{\overline{i\alpha}}}{\mathrm{D}t} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_\mathrm{f}\,. \tag{7.35}$$

For porous medium analysis, it is appropriate to consider velocities relative to the solid movement. Thus we make use of the identity

$$\frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t} = \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} + \left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right)\cdot\nabla \tag{7.36}$$

and apply this to the last three derivatives in Eq. (7.35), the derivatives of quantities that do not appear in the conservation or entropy balance equations, to obtain

$$\frac{\mathrm{D}^{\overline{i\alpha}}E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{i\alpha}}\eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}$$
$$- \eta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{s}}\theta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} + \frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}X^{\overline{\overline{i\alpha}}})}{\mathrm{D}t} - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\frac{\mathrm{D}^{\overline{s}}\mu^{\overline{i\alpha}}}{\mathrm{D}t}$$
$$- \left[\eta^{\overline{\overline{i\alpha}}}\nabla\theta^{\overline{\overline{i\alpha}}} - \nabla(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}X^{\overline{\overline{i\alpha}}}) + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right) = 0\,. \tag{7.37}$$

The multipliers of material derivatives based on the solid phase velocity can each be expressed as an average of a microscale quantity. Therefore, since the material derivatives are macroscale quantities, Equation (7.37) may be re-expressed using the averaging operator notation such that

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{i\alpha}}E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{i\alpha}}\eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} \\
&\quad - \left\langle \eta_{i\alpha}\frac{\mathrm{D}^{\overline{s}}\theta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} + \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\langle p_\alpha X_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}^{\overline{s}}\mu^{\overline{i\alpha}}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} \\
&\quad - \left[\eta^{\overline{\overline{i\alpha}}}\nabla\theta^{\overline{\overline{i\alpha}}} - \nabla(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}X^{\overline{\overline{i\alpha}}}) + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right) = 0\,. \qquad (7.38)
\end{aligned}
$$

The microscale Gibbs-Duhem equation for a chemical species in a fluid phase is given by Eq. (3.175). If the differentials in this equation are replaced by $\mathrm{D}^{\overline{s}}/\mathrm{D}t$, the result is

$$
\eta_{i\alpha}\frac{\mathrm{D}^{\overline{s}}\theta_\alpha}{\mathrm{D}t} - X_{i\alpha}\frac{\mathrm{D}^{\overline{s}}p_\alpha}{\mathrm{D}t} + \rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}^{\overline{s}}\mu_{i\alpha}}{\mathrm{D}t} - \rho_\alpha\omega_{i\alpha}\left(\frac{\mathrm{D}^{\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}\right)\Bigg|_{p_\alpha,\theta_\alpha} = 0
$$
$$
\text{for } i\in\mathcal{J}_s, \alpha\in\mathcal{J}_\mathrm{f}\,. \qquad (7.39)
$$

We apply the averaging operator to Eq. (7.39) and add the result to Eq. (7.38). After collecting terms, we have

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{i\alpha}}E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{i\alpha}}\eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} \\
&\quad + \left\langle \eta_{i\alpha}\frac{\mathrm{D}^{\overline{s}}(\theta_\alpha - \theta^{\overline{\overline{i\alpha}}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} + \left\langle \rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}^{\overline{s}}(\mu_{i\alpha} - \mu^{\overline{i\alpha}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} \\
&\quad + \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\langle p_\alpha X_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \left\langle X_{i\alpha}\frac{\mathrm{D}^{\overline{s}}p_\alpha}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} \\
&\quad - \left[\eta^{\overline{\overline{i\alpha}}}\nabla\theta^{\overline{\overline{i\alpha}}} - \nabla(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}X^{\overline{\overline{i\alpha}}}) + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right) \\
&\quad - \left\langle \rho_\alpha\omega_{i\alpha}\left(\frac{\mathrm{D}^{\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}\right)\Bigg|_{p_\alpha,\theta_\alpha}\right\rangle_{\Omega_\alpha,\Omega} = 0\,. \qquad (7.40)
\end{aligned}
$$

Application of the product rule to $X_{i\alpha}\mathrm{D}^{\overline{s}}p_\alpha/\mathrm{D}t$ yields

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{i\alpha}}E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{i\alpha}}\eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} \\
&\quad + \left\langle \eta_{i\alpha}\frac{\mathrm{D}^{\overline{s}}(\theta_\alpha - \theta^{\overline{\overline{i\alpha}}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} + \left\langle \rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}^{\overline{s}}(\mu_{i\alpha} - \mu^{\overline{i\alpha}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} \\
&\quad + \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\langle p_\alpha X_{i\alpha}\rangle_{\Omega_\alpha,\Omega} - \left\langle \frac{\mathrm{D}^{\overline{s}}(p_\alpha X_{i\alpha})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} + \left\langle p_\alpha\frac{\mathrm{D}^{\overline{s}}X_{i\alpha}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} \\
&\quad - \left[\eta^{\overline{\overline{i\alpha}}}\nabla\theta^{\overline{\overline{i\alpha}}} - \nabla(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}X^{\overline{\overline{i\alpha}}}) + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right)
\end{aligned}
$$

$$-\left\langle \rho_\alpha \omega_{i\alpha} \left(\frac{\mathrm{D}^{\overline{s}} \mu_{i\alpha}}{\mathrm{D}t} \right)\Bigg|_{p_\alpha,\theta_\alpha} \right\rangle_{\Omega_\alpha,\Omega} = 0\,. \tag{7.41}$$

Observe that a difference in material derivatives can be expanded to show that

$$\begin{aligned}\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\langle f_\alpha\rangle_{\Omega_\alpha,\Omega} - \left\langle \frac{\mathrm{D}^{\overline{s}} f_\alpha}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} &= \frac{\partial}{\partial t}\langle f_\alpha\rangle_{\Omega_\alpha,\Omega} + \mathbf{v}^{\overline{s}}\cdot\nabla\langle f_\alpha\rangle_{\Omega_\alpha,\Omega} \\ &- \left\langle \frac{\partial f_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} - \mathbf{v}^{\overline{s}}\cdot\langle \nabla f_\alpha\rangle_{\Omega_\alpha,\Omega} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}}\,. \end{aligned} \tag{7.42}$$

Averaging theorems T[3,(3,0),0] and G[3,(3,0),0] from Table 6.1 are applied to the last two terms in this equation, respectively. The resulting identity is the theorem

$$\begin{aligned}\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\langle f_\alpha\rangle_{\Omega_\alpha,\Omega} - \left\langle \frac{\mathrm{D}^{\overline{s}} f_\alpha}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} &= \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}}\right) f_\alpha \right\rangle_{\Omega_\kappa,\Omega} \\ &+ \frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}}\ \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{-}} \left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}}\right) f_\alpha^{*} \right\rangle_{\Omega_\kappa,\Omega} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}}\,. \end{aligned} \tag{7.43}$$

Application of this theorem in Eq. (7.41), where $f_\alpha = p_\alpha X_{i\alpha}$, and assuming that the fluid does not support a concentrated pressure function on its surface so that $p_\alpha^{*} = 0$, results in

$$\begin{aligned}\mathcal{T}_{*}^{\overline{\overline{i\alpha}}} := {} & \frac{\mathrm{D}^{\overline{i\alpha}} E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}} \frac{\mathrm{D}^{\overline{i\alpha}} \eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}})}{\mathrm{D}t} \\ & + \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}}\right) p_\alpha X_{i\alpha} \right\rangle_{\Omega_\kappa,\Omega} \\ & + \left\langle \eta_{i\alpha} \frac{\mathrm{D}^{\overline{s}} (\theta_\alpha - \theta^{\overline{\overline{i\alpha}}})}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} + \left\langle \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}^{\overline{s}} (\mu_{i\alpha} - \mu^{\overline{i\alpha}})}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} \\ & + \left\langle p_\alpha \frac{\mathrm{D}^{\overline{s}} X_{i\alpha}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha \omega_{i\alpha} \left(\frac{\mathrm{D}^{\overline{s}} \mu_{i\alpha}}{\mathrm{D}t} \right)\Bigg|_{p_\alpha,\theta_\alpha} \right\rangle_{\Omega_\alpha,\Omega} \\ & - \left[\eta^{\overline{\overline{i\alpha}}} \nabla\theta^{\overline{\overline{i\alpha}}} - \nabla(\varepsilon^{\overline{\overline{\alpha}}} p^\alpha X^{\overline{\overline{i\alpha}}}) + \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \nabla\mu^{\overline{i\alpha}} \right] \cdot \left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}} \right) = 0 \\ & \qquad\qquad\qquad\qquad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_{\mathrm{f}}\,. \end{aligned} \tag{7.44}$$

To make it easier to find this equation if performing a full TCAT analysis, a pointer to this defining equation for $\mathcal{T}_{*}^{\overline{\overline{i\alpha}}}$ is provided in Table 7.2.

Table 7.2 Macroscale dynamic equations for energy are located by the information in this table

Entity	**Basis**	$\mathcal{T}_*^{\overline{\overline{i\alpha}}}$ or $\mathcal{T}_*^{\overline{\overline{\alpha}}}$	$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}}$ or $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$
Phase	Species $i \in \mathfrak{I}_s$	Eq. (7.44)	Eq. (7.47)
$\alpha \in \mathfrak{I}_\mathrm{f}$	Entity	Eq. (7.54)	Eq. (7.58)
Solid	Species $i \in \mathfrak{I}_s$	Eq. (7.78)	Eq. (7.79)
$\alpha = s$	Entity	Eq. (7.80)	Eq. (7.81)
Interface	Species $i \in \mathfrak{I}_s$	Eq. (7.92)	Eq. (7.95)
$\alpha \in \mathfrak{I}_\mathrm{I}$	Entity	Eq. (7.96)	Eq. (7.97)
Curve	Species $i \in \mathfrak{I}_s$	Eq. (7.100)	Eq. (7.101)
$\alpha \in \mathfrak{I}_\mathrm{C}$	Entity	Eq. (7.102)	Eq. (7.103)

7.4.2 Fluid Species Potential Energy

A dynamic relation for the body force potential is also necessary. The macroscale potential is defined in Eq. (6.153). The material derivative of this expression is

$$\frac{\mathrm{D}^{\overline{i\alpha}}\Psi^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \psi^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}\psi^{\overline{i\alpha}}}{\mathrm{D}t} = 0\,. \tag{7.45}$$

Making use of the material derivative expansion in Eq. (7.36) to rewrite the last material derivative, we obtain

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{i\alpha}}\Psi^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \psi^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\frac{\mathrm{D}^{\overline{s}}\psi^{\overline{i\alpha}}}{\mathrm{D}t}\\ &\qquad - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right)\cdot\nabla\psi^{\overline{i\alpha}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{f}\,.\end{aligned} \tag{7.46}$$

Introduction of the averaging operator for the third material derivative on the left gives the final expression,

$$\begin{aligned}\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}} :=& \frac{\mathrm{D}^{\overline{i\alpha}}\Psi^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \psi^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} - \left\langle \rho_{\alpha}\omega_{i\alpha}\frac{\mathrm{D}^{\overline{s}}\psi^{\overline{i\alpha}}}{\mathrm{D}t}\right\rangle_{\Omega_i,\Omega}\\ &\qquad - \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right)\cdot\nabla\psi^{\overline{i\alpha}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{f}\,.\end{aligned} \tag{7.47}$$

This equation is pointed to in Table 7.2.

7.4.3 *Fluid-phase Energy*

The macroscale Euler equation for the fluid phase was obtained as Eq. (7.13) and is also compiled in Table 7.1. The material derivative of this energy function taken making use of the entity velocity is

$$\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}$$
$$- \eta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\theta^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + \frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha})}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}\mu^{\overline{i\alpha}}}{\mathrm{D}t} = 0 \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{f}}\,. \tag{7.48}$$

Applying the identity

$$\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t} = \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} + \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)\cdot\nabla \tag{7.49}$$

to the derivatives of temperature, pressure, and chemical potential allows Eq. (7.48) to be rewritten as

$$\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} - \eta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{s}}\theta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}$$
$$+ \frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha})}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\frac{\mathrm{D}^{\overline{s}}\mu^{\overline{i\alpha}}}{\mathrm{D}t}$$
$$- \left[\eta^{\overline{\overline{\alpha}}}\nabla\theta^{\overline{\overline{\alpha}}} - \nabla(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}) + \sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) = 0\,. \tag{7.50}$$

As with the species version, selectively introducing the averaging operator back into this equation yields

$$\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} - \left\langle\eta_{\alpha}\frac{\mathrm{D}^{\overline{s}}\theta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}$$
$$+ \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\langle p_{\alpha}\rangle_{\Omega_\alpha,\Omega} - \sum_{i\in\mathfrak{I}_s}\left\langle\rho_{\alpha}\omega_{i\alpha}\frac{\mathrm{D}^{\overline{s}}\mu^{\overline{i\alpha}}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}$$
$$- \left[\eta^{\overline{\overline{\alpha}}}\nabla\theta^{\overline{\overline{\alpha}}} - \nabla(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}) + \sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) = 0\,. \tag{7.51}$$

The material derivative of the microscale Gibbs-Duhem Eq. (3.43) is

$$0 = \eta_{\alpha}\frac{\mathrm{D}^{\overline{s}}\theta_{\alpha}}{\mathrm{D}t} - \frac{\mathrm{D}^{\overline{s}}p_{\alpha}}{\mathrm{D}t} + \sum_{i\in\mathfrak{I}_s}\rho_{\alpha}\omega_{i\alpha}\frac{\mathrm{D}^{\overline{s}}\mu_{i\alpha}}{\mathrm{D}t} \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{f}}\,. \tag{7.52}$$

Application of the averaging operator to Eq. (7.52) followed by addition to Eq. (7.51) yields

$$\begin{aligned}
&\frac{\mathrm{D}^{\overline{\alpha}} E^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}} \frac{\mathrm{D}^{\overline{\alpha}} \eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \sum_{i \in \mathfrak{I}_s} \mu^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}})}{\mathrm{D}t} + \left\langle \eta_\alpha \frac{\mathrm{D}^{\overline{s}} (\theta_\alpha - \theta^{\overline{\overline{\alpha}}})}{\mathrm{D}t} \right\rangle_{\Omega_\alpha, \Omega} \\
&\quad + \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \langle p_\alpha \rangle_{\Omega_\alpha, \Omega} - \left\langle \frac{\mathrm{D}^{\overline{s}} p_\alpha}{\mathrm{D}t} \right\rangle_{\Omega_\alpha, \Omega} + \sum_{i \in \mathfrak{I}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{i\alpha} - \mu^{\overline{i\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\alpha, \Omega} \\
&\quad - \left[\eta^{\overline{\overline{\alpha}}} \nabla \theta^{\overline{\overline{\alpha}}} - \nabla (\varepsilon^{\overline{\overline{\alpha}}} p^{\alpha}) + \sum_{i \in \mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \nabla \mu^{\overline{i\alpha}} \right] \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right) = 0 \, . \qquad (7.53)
\end{aligned}$$

Finally, the averaging theorem relation given by Eq. (7.43) may be used with $f_\alpha = p_\alpha$ to obtain the dynamic equation

$$\begin{aligned}
\mathcal{T}_*^{\overline{\overline{\alpha}}} :=\ & \frac{\mathrm{D}^{\overline{\alpha}} E^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}} \frac{\mathrm{D}^{\overline{\alpha}} \eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \sum_{i \in \mathfrak{I}_s} \mu^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}})}{\mathrm{D}t} \\
& + \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\alpha}} \left\langle \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) p_\alpha \right\rangle_{\Omega_\kappa, \Omega} \\
& + \left\langle \eta_\alpha \frac{\mathrm{D}^{\overline{s}} (\theta_\alpha - \theta^{\overline{\overline{\alpha}}})}{\mathrm{D}t} \right\rangle_{\Omega_\alpha, \Omega} + \sum_{i \in \mathfrak{I}_s} \left\langle \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{i\alpha} - \mu^{\overline{i\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_\alpha, \Omega} \\
& - \left[\eta^{\overline{\overline{\alpha}}} \nabla \theta^{\overline{\overline{\alpha}}} - \nabla (\varepsilon^{\overline{\overline{\alpha}}} p^{\alpha}) + \sum_{i \in \mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \nabla \mu^{\overline{i\alpha}} \right] \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right) = 0 \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} \, .
\end{aligned} \qquad (7.54)$$

It is important to note that Eq. (7.54) may alternatively be obtained by summing Eq. (7.44) over all species, proving that

$$\mathcal{T}_*^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathcal{T}_*^{\overline{\overline{i\alpha}}} \, . \qquad (7.55)$$

The proof of this relation is left as an exercise.

7.4.4 Fluid-phase Potential Energy

Based on Eqs. (6.153) and (6.161), the macroscale body force potential is defined such that

$$\Psi^{\overline{\overline{\alpha}}} - \sum_{i \in \mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \psi^{\overline{i\alpha}} = 0 \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} \, . \qquad (7.56)$$

The material derivative of this expression based on the entity velocity is

$$\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s} \psi^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}} \frac{\mathrm{D}^{\overline{\alpha}}\psi^{\overline{i\alpha}}}{\mathrm{D}t} = 0\,. \tag{7.57}$$

Making use of Eq. (7.49) and introducing the averaging operator, we then obtain

$$\begin{aligned}\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}} := \frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t} &- \sum_{i\in\mathfrak{I}_s} \psi^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t} - \sum_{i\in\mathfrak{I}_s} \left\langle \rho_{\alpha}\omega_{i\alpha} \frac{\mathrm{D}^{\overline{s}}\psi^{\overline{i\alpha}}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} \\ &- \sum_{i\in\mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}} \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) \cdot \nabla\psi^{\overline{i\alpha}} = 0 \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}}\,. \end{aligned} \tag{7.58}$$

This equation is noted in Table 7.2.

7.5 Solid-phase Energy Dynamics

The derivation of the dynamic conditions for a solid phase follows the same lines as for a fluid phase but is somewhat complicated by the stress representation of an elastic solid. Therefore, a full derivation follows for the species-based equation. The dynamic condition for the phase-based equation can be obtained from this result.

7.5.1 Solid Species Energy

The macroscale Euler equation for a species in a solid phase has been obtained from the microscale form, Eq. (3.182), and is provided in Table 7.1. The material derivative of this equation calculated with the velocity of the species as the observation velocity is

$$\begin{aligned}\frac{\mathrm{D}^{\overline{is}}E^{\overline{\overline{is}}}}{\mathrm{D}t} &- \theta^{\overline{\overline{is}}} \frac{\mathrm{D}^{\overline{is}}\eta^{\overline{\overline{is}}}}{\mathrm{D}t} - \mu^{\overline{is}} \frac{\mathrm{D}^{\overline{is}}(\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}})}{\mathrm{D}t} - \eta^{\overline{\overline{is}}} \frac{\mathrm{D}^{\overline{is}}\theta^{\overline{\overline{is}}}}{\mathrm{D}t} \\ &- \frac{\mathrm{D}^{\overline{is}}}{\mathrm{D}t}\left(\varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}} : \frac{\mathbf{X}^{\overline{\overline{is}}}\cdot\mathbf{C}^{s}}{j^{s}}\right) - \varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}} \frac{\mathrm{D}^{\overline{is}}\mu^{\overline{is}}}{\mathrm{D}t} = 0 \quad \text{for } i \in \mathfrak{I}_s\,. \end{aligned} \tag{7.59}$$

Examination of Eq. (7.59) reveals that the first three material derivatives are of a form consistent with terms arising in the conservation and balance equations. The remaining three material derivative terms have no counterparts in the conservation and balance equations. Because we anticipate that the most useful form of the dynamic species energy equation will include the first three material derivatives but be void of the last three material derivative expressions, further manipulations are needed. In short, we are seeking a form of Eq. (7.59) that has components of a force-flux form other than material derivatives that can easily be made to vanish.

This objective motivates the substantial manipulations detailed below that lead to the desired form of the dynamic condition.

Making use of the identity given in Eq. (7.36) with α replaced by s, we change the last three material derivatives in Eq. (7.59) so that they are relative to the solid phase macroscale velocity. The result is

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{is}}E^{\overline{\overline{is}}}}{\mathrm{D}t}-\theta^{\overline{\overline{is}}}\frac{\mathrm{D}^{\overline{is}}\eta^{\overline{\overline{is}}}}{\mathrm{D}t}-\mu^{\overline{is}}\frac{\mathrm{D}^{\overline{is}}(\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}})}{\mathrm{D}t}-\eta^{\overline{\overline{is}}}\frac{\mathrm{D}^{\overline{s}}\theta^{\overline{\overline{is}}}}{\mathrm{D}t}\\&\quad-\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(\varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}:\frac{\mathbf{X}^{\overline{\overline{is}}}\cdot\mathbf{C}^{s}}{j^{s}}\right)-\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}}\frac{\mathrm{D}^{\overline{s}}\mu^{\overline{is}}}{\mathrm{D}t}\\&\quad-\left[\eta^{\overline{\overline{is}}}\nabla\theta^{\overline{\overline{is}}}+\nabla\left(\varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}:\frac{\mathbf{X}^{\overline{\overline{is}}}\cdot\mathbf{C}^{s}}{j^{s}}\right)+\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}}\nabla\mu^{\overline{is}}\right]\cdot\left(\mathbf{v}^{\overline{is}}-\mathbf{v}^{\overline{s}}\right)=0\,. \qquad (7.60)\end{aligned}$$

The fourth through sixth terms may now be re-expressed by introducing the averaging operator, $\langle\cdot\rangle_{\Omega_s,\Omega}$, in anticipation of making use of the microscale Gibbs-Duhem equation. With this equivalent notation, we obtain

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{is}}E^{\overline{\overline{is}}}}{\mathrm{D}t}-\theta^{\overline{\overline{is}}}\frac{\mathrm{D}^{\overline{is}}\eta^{\overline{\overline{is}}}}{\mathrm{D}t}-\mu^{\overline{is}}\frac{\mathrm{D}^{\overline{is}}(\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}})}{\mathrm{D}t}-\left\langle\eta_{is}\frac{\mathrm{D}^{\overline{s}}\theta^{\overline{\overline{is}}}}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}\\&\quad-\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left\langle\sigma_{s}:\frac{\mathbf{X}_{is}\cdot\mathbf{C}_{s}}{j_{s}}\right\rangle_{\Omega_s,\Omega}-\left\langle\rho_{s}\omega_{is}\frac{\mathrm{D}^{\overline{s}}\mu^{\overline{is}}}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}\\&\quad-\left[\eta^{\overline{\overline{is}}}\nabla\theta^{\overline{\overline{is}}}+\nabla\left(\varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}:\frac{\mathbf{X}^{\overline{\overline{is}}}\cdot\mathbf{C}^{s}}{j^{s}}\right)+\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}}\nabla\mu^{\overline{is}}\right]\cdot\left(\mathbf{v}^{\overline{is}}-\mathbf{v}^{\overline{s}}\right)=0\,. \qquad (7.61)\end{aligned}$$

As a prelude to further work on Eq. (7.61), we express the microscopic Gibbs-Duhem equation, Eq. (3.188), in terms of the material derivative making use of the macroscale solid phase velocity so that

$$\eta_{is}\frac{\mathrm{D}^{\overline{s}}\theta_{s}}{\mathrm{D}t}+\mathbf{X}_{is}\cdot\frac{\mathbf{C}_{s}}{j_{s}}:\frac{\mathrm{D}^{\overline{s}}\sigma_{s}}{\mathrm{D}t}+\rho_{s}\omega_{is}\frac{\mathrm{D}^{\overline{s}}\mu_{is}}{\mathrm{D}t}-\rho_{s}\omega_{is}\left(\frac{\mathrm{D}^{\overline{s}}\mu_{is}}{\mathrm{D}t}\right)\bigg|_{\sigma_s,\theta_s}=0 \quad \text{for } i\in\mathfrak{I}_{s}\,. \qquad (7.62)$$

Making use of the product rule to rearrange the second term in this equation and averaging the result using the operator $\langle\cdot\rangle_{\Omega_s,\Omega}$, we obtain

$$\begin{aligned}&\left\langle\eta_{is}\frac{\mathrm{D}^{\overline{s}}\theta_{s}}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}+\left\langle\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(\sigma_{s}:\frac{\mathbf{X}_{is}\cdot\mathbf{C}_{s}}{j_{s}}\right)\right\rangle_{\Omega_s,\Omega}-\left\langle\sigma_{s}:\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_{s}}{j_{s}}\right)\right\rangle_{\Omega_s,\Omega}\\&\quad+\left\langle\rho_{s}\omega_{is}\frac{\mathrm{D}^{\overline{s}}\mu_{is}}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}-\left\langle\rho_{s}\omega_{is}\left(\frac{\mathrm{D}^{\overline{s}}\mu_{is}}{\mathrm{D}t}\right)\bigg|_{\sigma_s,\theta_s}\right\rangle_{\Omega_s,\Omega}=0\,. \qquad (7.63)\end{aligned}$$

This equation may be added directly to Eq. (7.61). After collecting similar terms that are being averaged, we obtain

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{is}} E^{\overline{\overline{is}}}}{\mathrm{D}t} - \theta^{\overline{\overline{is}}} \frac{\mathrm{D}^{\overline{is}} \eta^{\overline{\overline{is}}}}{\mathrm{D}t} - \mu^{\overline{is}} \frac{\mathrm{D}^{\overline{is}} (\varepsilon^{\overline{\overline{s}}} \rho^s \omega^{i\overline{s}})}{\mathrm{D}t} \\
&\quad + \left\langle \eta_{is} \frac{\mathrm{D}^{\overline{s}} (\theta_s - \theta^{\overline{\overline{is}}})}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} + \left\langle \rho_s \omega_{is} \frac{\mathrm{D}^{\overline{s}} (\mu_{is} - \mu^{\overline{is}})}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} \\
&\quad - \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left\langle \boldsymbol{\sigma}_s : \frac{\mathsf{X}_{is} \cdot \mathsf{C}_s}{j_s} \right\rangle_{\Omega_s,\Omega} + \left\langle \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left(\boldsymbol{\sigma}_s : \frac{\mathsf{X}_{is} \cdot \mathsf{C}_s}{j_s} \right) \right\rangle_{\Omega_s,\Omega} \\
&\quad - \left\langle \boldsymbol{\sigma}_s : \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left(\mathsf{X}_{is} \cdot \frac{\mathsf{C}_s}{j_s} \right) \right\rangle_{\Omega_s,\Omega} \\
&\quad - \left[\eta^{\overline{\overline{is}}} \nabla \theta^{\overline{\overline{is}}} + \nabla \left(\varepsilon^{\overline{\overline{s}}} \boldsymbol{\sigma}^{\overline{\overline{s}}} : \frac{\mathsf{X}^{\overline{\overline{is}}} \cdot \mathsf{C}^s}{j^s} \right) + \varepsilon^{\overline{\overline{s}}} \rho^s \omega^{i\overline{s}} \nabla \mu^{\overline{is}} \right] \cdot \left(\mathbf{v}^{\overline{is}} - \mathbf{v}^{\overline{s}} \right) \\
&\quad - \left\langle \rho_s \omega_{is} \left(\frac{\mathrm{D}^{\overline{s}} \mu_{is}}{\mathrm{D}t} \right) \bigg|_{\boldsymbol{\sigma}_s, \theta_s} \right\rangle_{\Omega_s,\Omega} = 0\,.
\end{aligned}
\tag{7.64}
$$

We make use of the theorem given by Eq. (7.43) with $\alpha = s$ and $f_\alpha = \boldsymbol{\sigma}_s : \mathsf{X}_{is} \cdot \mathsf{C}_s / j_s$ to obtain

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left\langle \boldsymbol{\sigma}_s : \frac{\mathsf{X}_{is} \cdot \mathsf{C}_s}{j_s} \right\rangle_{\Omega_s,\Omega} - \left\langle \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left(\boldsymbol{\sigma}_s : \frac{\mathsf{X}_{is} \cdot \mathsf{C}_s}{j_s} \right) \right\rangle_{\Omega_s,\Omega} \\
&\quad = \sum_{\kappa \in \mathfrak{J}_{\mathrm{cs}}} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \boldsymbol{\sigma}_s : \frac{\mathsf{X}_{is} \cdot \mathsf{C}_s}{j_s} \right\rangle_{\Omega_\kappa,\Omega} \\
&\quad + \frac{1}{2} \sum_{\beta \in \mathfrak{J}^-_{\mathrm{cs}}} \sum_{\kappa \in \mathfrak{J}^-_{\mathrm{c}\beta}} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \boldsymbol{\sigma}^*_s : \frac{\mathsf{X}_{is} \cdot \mathsf{C}_s}{j_s} \right\rangle_{\Omega_\kappa,\Omega} ,
\end{aligned}
\tag{7.65}
$$

where we have allowed for the possibility that the solid phase may sustain a concentrated stress at a common curve on its surface. Substitution of Eq. (7.65) into Eq. (7.64) yields

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{is}} E^{\overline{\overline{is}}}}{\mathrm{D}t} - \theta^{\overline{\overline{is}}} \frac{\mathrm{D}^{\overline{is}} \eta^{\overline{\overline{is}}}}{\mathrm{D}t} - \mu^{\overline{is}} \frac{\mathrm{D}^{\overline{is}} (\varepsilon^{\overline{\overline{s}}} \rho^s \omega^{i\overline{s}})}{\mathrm{D}t} - \sum_{\kappa \in \mathfrak{J}_{\mathrm{cs}}} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \boldsymbol{\sigma}_s : \frac{\mathsf{X}_{is} \cdot \mathsf{C}_s}{j_s} \right\rangle_{\Omega_\kappa,\Omega} \\
&\quad - \frac{1}{2} \sum_{\beta \in \mathfrak{J}^-_{\mathrm{cs}}} \sum_{\kappa \in \mathfrak{J}^-_{\mathrm{c}\beta}} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right) \boldsymbol{\sigma}^*_s : \frac{\mathsf{X}_{is} \cdot \mathsf{C}_s}{j_s} \right\rangle_{\Omega_\kappa,\Omega} + \left\langle \eta_{is} \frac{\mathrm{D}^{\overline{s}} (\theta_s - \theta^{\overline{\overline{is}}})}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} \\
&\quad + \left\langle \rho_s \omega_{is} \frac{\mathrm{D}^{\overline{s}} (\mu_{is} - \mu^{\overline{is}})}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} - \left\langle \boldsymbol{\sigma}_s : \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left(\mathsf{X}_{is} \cdot \frac{\mathsf{C}_s}{j_s} \right) \right\rangle_{\Omega_s,\Omega}
\end{aligned}
$$

$$
\begin{aligned}
&- \left\langle \rho_s \omega_{is} \left(\frac{\mathrm{D}^{\overline{s}} \mu_{is}}{\mathrm{D}t} \right) \Big|_{\sigma_s, \theta_s} \right\rangle_{\Omega_s, \Omega} \\
&- \left[\eta^{\overline{\overline{is}}} \nabla \theta^{\overline{\overline{is}}} + \nabla \left(\varepsilon^{\overline{\overline{s}}} \sigma^{\overline{\overline{s}}} : \frac{\mathbf{X}^{\overline{\overline{is}}} \cdot \mathbf{C}^s}{j^s} \right) + \varepsilon^{\overline{\overline{s}}} \rho^s \omega^{i\overline{s}} \nabla \mu^{\overline{is}} \right] \cdot \left(\mathbf{v}^{\overline{is}} - \mathbf{v}^{\overline{s}} \right) = 0 \,. \qquad (7.66)
\end{aligned}
$$

Some additional advantage for subsequent study can be gained by rearranging the material derivative of $\mathbf{X}_{is} \cdot \mathbf{C}_s / j_s$.

We make use of the identity

$$
\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} = \frac{\mathrm{D}_s}{\mathrm{D}t} - \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \cdot \nabla \qquad (7.67)
$$

to show that

$$
\begin{aligned}
\left\langle \sigma_s : \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right\rangle_{\Omega_s, \Omega} &= \left\langle \sigma_s : \frac{\mathrm{D}_s}{\mathrm{D}t} \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right\rangle_{\Omega_s, \Omega} \\
&- \left\langle \sigma_s : \left[\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \cdot \nabla \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right] \right\rangle_{\Omega_s, \Omega} . \qquad (7.68)
\end{aligned}
$$

Application of the product rule to the derivatives that appear on the right side of this equation yields

$$
\begin{aligned}
\left\langle \sigma_s : \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right\rangle_{\Omega_s, \Omega} &= \left\langle \sigma_s : \left[\frac{\mathrm{D}_s \mathbf{X}_{is}}{\mathrm{D}t} \cdot \left(\frac{\mathbf{C}_s}{j_s} \right) \right] \right\rangle_{\Omega_s, \Omega} \\
&+ \left\langle \sigma_s : \left[\mathbf{X}_{is} \cdot \frac{\mathrm{D}_s \mathbf{C}_s}{\mathrm{D}t} \left(\frac{1}{j_s} \right) \right] \right\rangle_{\Omega_s, \Omega} + \left\langle \sigma_s : \left[\mathbf{X}_{is} \cdot \mathbf{C}_s \frac{\mathrm{D}_s}{\mathrm{D}t} \left(\frac{1}{j_s} \right) \right] \right\rangle_{\Omega_s, \Omega} \\
&- \left\langle \nabla \cdot \left[\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \sigma_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right] \right\rangle_{\Omega_s, \Omega} \\
&+ \left\langle \nabla \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \left[\sigma_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right] \right\rangle_{\Omega_s, \Omega} \\
&+ \left\langle \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \cdot \nabla \sigma_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right\rangle_{\Omega_s, \Omega} . \qquad (7.69)
\end{aligned}
$$

Substitution of the identities [1]

$$
\frac{\mathrm{D}_s}{\mathrm{D}t} \left(\frac{1}{j_s} \right) = -\frac{1}{j_s} \mathbf{I} : \mathbf{d}_s \qquad (7.70)
$$

and

$$
\frac{\mathrm{D}_s \mathbf{C}_s}{\mathrm{D}t} = 2 \left(\nabla_X \mathbf{x}_s \right) \cdot \mathbf{d}_s \cdot \left(\nabla_X \mathbf{x}_s \right)^{\mathrm{T}} \qquad (7.71)
$$

into Eq. (7.69) provides

$$\begin{aligned}\left\langle \sigma_s : \frac{\mathrm{D}^{\bar{s}}}{\mathrm{D}t}\left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Omega_s,\Omega} &= \left\langle \sigma_s : \left[\frac{\mathrm{D}_s\mathbf{X}_{is}}{\mathrm{D}t}\cdot\left(\frac{\mathbf{C}_s}{j_s}\right)\right]\right\rangle_{\Omega_s,\Omega} \\ &+ \left\langle \left[\frac{2}{j_s}\left(\nabla_X\mathbf{x}_s\right)^{\mathrm{T}}\cdot\sigma_s\cdot\mathbf{X}_{is}\cdot\left(\nabla_X\mathbf{x}_s\right)\right] : \mathbf{d}_s\right\rangle_{\Omega_s,\Omega} \\ &- \left\langle \sigma_s : \left[\mathbf{X}_{is}\cdot\mathbf{C}_s\frac{1}{j_s}\mathbf{l}:\mathbf{d}_s\right]\right\rangle_{\Omega_s,\Omega} - \left\langle \nabla\cdot\left[\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\sigma_s : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\right]\right\rangle_{\Omega_s,\Omega} \\ &+ \left\langle \left(\mathbf{l}:\mathbf{d}_s-\mathbf{l}:\mathbf{d}^{\bar{\bar{s}}}\right)\left[\sigma_s : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\right]\right\rangle_{\Omega_s,\Omega} \\ &+ \left\langle \left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\cdot\nabla\sigma_s : \left[\left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\right]\right\rangle_{\Omega_s,\Omega} .\end{aligned} \tag{7.72}$$

In writing this equation, use has been made of the previously established definitions of the rate of strain tensors with $\nabla\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right) = \mathbf{l}:\mathbf{d}_s-\mathbf{l}:\mathbf{d}^{\bar{\bar{s}}}$. The microscale species stress tensor may be designated $\mathbf{t}_{is}$, where

$$\mathbf{t}_{is} = \frac{2}{j_s}\left(\nabla_X\mathbf{x}_s\right)^{\mathrm{T}}\cdot\sigma_s\cdot\mathbf{X}_{is}\cdot\left(\nabla_X\mathbf{x}_s\right) . \tag{7.73}$$

Incorporating this definition into Eq. (7.72) and rearranging terms gives

$$\begin{aligned}\left\langle \sigma_s : \frac{\mathrm{D}^{\bar{s}}}{\mathrm{D}t}\left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\right\rangle_{\Omega_s,\Omega} &= \left\langle \sigma_s : \left[\frac{\mathrm{D}_s\mathbf{X}_{is}}{\mathrm{D}t}\cdot\left(\frac{\mathbf{C}_s}{j_s}\right)\right]\right\rangle_{\Omega_s,\Omega} \\ &+ \left\langle \nabla\cdot\left\{\left[\mathbf{t}_{is}-\sigma_s : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\mathbf{l}\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\}\right\rangle_{\Omega_s,\Omega} \\ &- \left\langle \left[\sigma_s : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\mathbf{l}-\mathbf{t}_{is}\right] : \mathbf{d}^{\bar{\bar{s}}}\right\rangle_{\Omega_s,\Omega} \\ &- \left\langle \left[\nabla\cdot\mathbf{t}_{is}-\nabla\sigma_s : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_s,\Omega} .\end{aligned} \tag{7.74}$$

Theorem D[3,(3,0),0] from Table 6.1 may be applied to the second term on the right side of Eq. (7.74) to show that

$$\begin{aligned}&\left\langle \nabla\cdot\left\{\left[\mathbf{t}_{is}-\sigma_s : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\mathbf{l}\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\}\right\rangle_{\Omega_s,\Omega} \\ &\quad= \nabla\cdot\left\langle \left[\mathbf{t}_{is}-\sigma_s : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\mathbf{l}\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_s,\Omega} \\ &\quad+ \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}s}} \left\langle \mathbf{n}_s\cdot\left[\mathbf{t}_{is}-\sigma_s : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\mathbf{l}\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_\kappa,\Omega} \\ &\quad+ \frac{1}{2}\sum_{\beta\in\mathfrak{I}_{\mathrm{c}s}^{-}}\ \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\beta}^{-}} \left\langle \mathbf{n}_s\cdot\left[\mathbf{t}_{is}^{*}-\sigma_s^{*} : \left(\mathbf{X}_{is}\cdot\frac{\mathbf{C}_s}{j_s}\right)\mathbf{l}\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_\kappa,\Omega} .\end{aligned} \tag{7.75}$$

Additionally, we note that

$$\left\langle \left[\sigma_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \mathbf{I} - \mathbf{t}_{is} \right] : \mathbf{d}^{\overline{\overline{s}}} \right\rangle_{\Omega_s,\Omega} = \varepsilon^{\overline{\overline{s}}} \sigma^{\overline{\overline{s}}} : \left(\mathbf{X}^{\overline{\overline{is}}} \cdot \frac{\mathbf{C}^s}{j^s} \right) \mathbf{I} : \mathbf{d}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}} \mathbf{t}^{is} : \mathbf{d}^{\overline{\overline{s}}} \,. \tag{7.76}$$

Substituting these last two equalities into Eq. (7.74) gives us

$$\begin{aligned}
\left\langle \sigma_s : \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right\rangle_{\Omega_s,\Omega} &= \left\langle \sigma_s : \left[\frac{\mathrm{D}_s \mathbf{X}_{is}}{\mathrm{D}t} \cdot \left(\frac{\mathbf{C}_s}{j_s} \right) \right] \right\rangle_{\Omega_s,\Omega} \\
&+ \nabla \cdot \left\langle \left[\mathbf{t}_{is} - \sigma_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \mathbf{I} \right] \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s,\Omega} \\
&+ \sum_{\kappa \in \mathfrak{J}_{\mathrm{c}s}} \left\langle \mathbf{n}_s \cdot \left[\mathbf{t}_{is} - \sigma_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \mathbf{I} \right] \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\kappa,\Omega} \\
&+ \frac{1}{2} \sum_{\beta \in \mathfrak{J}^-_{\mathrm{c}s}} \sum_{\kappa \in \mathfrak{J}^-_{\mathrm{c}\beta}} \left\langle \mathbf{n}_s \cdot \left[\mathbf{t}^*_{is} - \sigma^*_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \mathbf{I} \right] \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\kappa,\Omega} \\
&- \varepsilon^{\overline{\overline{s}}} \sigma^{\overline{\overline{s}}} : \left(\mathbf{X}^{\overline{\overline{is}}} \cdot \frac{\mathbf{C}^s}{j^s} \right) \mathbf{I} : \mathbf{d}^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{s}}} \mathbf{t}^{is} : \mathbf{d}^{\overline{\overline{s}}} \\
&- \left\langle \left[\nabla \cdot \mathbf{t}_{is} - \nabla \sigma_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \right] \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s,\Omega} \,.
\end{aligned} \tag{7.77}$$

Finally, substituting Eq. (7.77) back into Eq. (7.66) and rearranging the terms provides

$$\begin{aligned}
\mathcal{T}^{\overline{\overline{is}}}_* :=& \frac{\mathrm{D}^{\overline{is}} E^{\overline{\overline{is}}}}{\mathrm{D}t} - \theta^{\overline{\overline{is}}} \frac{\mathrm{D}^{\overline{is}} \eta^{\overline{\overline{is}}}}{\mathrm{D}t} - \mu^{\overline{is}} \frac{\mathrm{D}^{\overline{is}} \left(\varepsilon^{\overline{\overline{s}}} \rho^s \omega^{i\overline{s}} \right)}{\mathrm{D}t} \\
&- \sum_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_\kappa - \mathbf{v}_s \right) \sigma_s : \frac{\mathbf{X}_{is} \cdot \mathbf{C}_s}{j_s} \right\rangle_{\Omega_\kappa,\Omega} - \sum_{\kappa \in \mathfrak{J}_{\mathrm{c}s}} \left\langle \mathbf{n}_s \cdot \mathbf{t}_{is} \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\kappa,\Omega} \\
&- \frac{1}{2} \sum_{\beta \in \mathfrak{J}^-_{\mathrm{c}s}} \sum_{\kappa \in \mathfrak{J}^-_{\mathrm{c}\beta}} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_\kappa - \mathbf{v}_s \right) \sigma^*_s : \frac{\mathbf{X}_{is} \cdot \mathbf{C}_s}{j_s} \right\rangle_{\Omega_\kappa,\Omega} \\
&- \frac{1}{2} \sum_{\beta \in \mathfrak{J}^-_{\mathrm{c}s}} \sum_{\kappa \in \mathfrak{J}^-_{\mathrm{c}\beta}} \left\langle \mathbf{n}_s \cdot \mathbf{t}^*_{is} \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_\kappa,\Omega} + \left\langle \eta_{is} \frac{\mathrm{D}^{\overline{s}} \left(\theta_s - \theta^{\overline{\overline{is}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} \\
&+ \left\langle \rho_s \omega_{is} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{is} - \mu^{\overline{is}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} - \left\langle \sigma_s : \left[\frac{\mathrm{D}_s \mathbf{X}_{is}}{\mathrm{D}t} \cdot \left(\frac{\mathbf{C}_s}{j_s} \right) \right] \right\rangle_{\Omega_s,\Omega} \\
&- \left\langle \rho_s \omega_{is} \left. \left(\frac{\mathrm{D}^{\overline{s}} \mu_{is}}{\mathrm{D}t} \right) \right|_{\sigma_s,\theta_s} \right\rangle_{\Omega_s,\Omega} - \nabla \cdot \left\langle \left[\mathbf{t}_{is} - \sigma_s : \left(\mathbf{X}_{is} \cdot \frac{\mathbf{C}_s}{j_s} \right) \mathbf{I} \right] \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s,\Omega} \\
&- \varepsilon^{\overline{\overline{s}}} \mathbf{t}^{is} : \mathbf{d}^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{s}}} \sigma^{\overline{\overline{s}}} : \left(\mathbf{X}^{\overline{\overline{is}}} \cdot \frac{\mathbf{C}^s}{j^s} \right) \mathbf{I} : \mathbf{d}^{\overline{\overline{s}}}
\end{aligned}$$

$$
\begin{aligned}
&+\left\langle\left[\nabla\cdot\mathsf{t}_{is}-\nabla\sigma_s:\left(\mathsf{X}_{is}\cdot\frac{\mathsf{C}_s}{j_s}\right)\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\\
&-\left[\eta^{\overline{\overline{is}}}\nabla\theta^{\overline{\overline{is}}}+\nabla\left(\varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}:\frac{\mathsf{X}^{\overline{\overline{is}}}\cdot\mathsf{C}^s}{j^s}\right)+\varepsilon^{\overline{\overline{s}}}\rho^s\omega^{i\overline{s}}\nabla\mu^{\overline{is}}\right]\cdot\left(\mathbf{v}^{\overline{is}}-\mathbf{v}^{\overline{s}}\right)=0\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{for } i\in\mathfrak{I}_s\,. \qquad (7.78)
\end{aligned}
$$

This equation is used when the energy of the solid is considered on a species basis. This equation number is entered in Table 7.2 for convenient reference.

7.5.2 Solid Species Potential Energy

The dynamic condition for the body force potential is the same as that for a fluid phase as given by Eq. (7.47) with $\alpha = s$ such that

$$
\begin{aligned}
\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{is}}} :=\ &\frac{\mathrm{D}^{\overline{is}}\Psi^{\overline{\overline{is}}}}{\mathrm{D}t}-\psi^{\overline{is}}\frac{\mathrm{D}^{\overline{is}}(\varepsilon^{\overline{\overline{s}}}\rho^s\omega^{i\overline{s}})}{\mathrm{D}t}-\left\langle\rho_s\omega_{is}\frac{\mathrm{D}^{\overline{s}}\psi^{\overline{is}}}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}\\
&-\varepsilon^{\overline{\overline{s}}}\rho^s\omega^{i\overline{s}}\left(\mathbf{v}^{\overline{is}}-\mathbf{v}^{\overline{s}}\right)\cdot\nabla\psi^{\overline{is}}=0 \quad \text{for } i\in\mathfrak{I}_s\,. \qquad (7.79)
\end{aligned}
$$

7.5.3 Solid-phase Energy

There are at least three ways to obtain the dynamic energy equations for the solid phase as a whole. The first is analogous to what was done for the species in Sect. 7.5.1. This involves starting with the Euler equation for the solid phase entity as found in Table 7.1, taking the material derivative (making use of the entity velocity), and manipulating the resultant form. The step-by-step derivation in Sect. 7.5.1 can be used as a guide. The second approach is to sum Eq. (7.78) over all species and make use of definitions of entity properties in terms of sums of species properties to arrive at the desired result. The third approach is to observe differences between Eqs. (7.44) and (7.54) for the fluid phase. We then can infer that a similar simplification will occur for the solid and simply write down the result. Although we have used all three methods with success, here we only present the third and write the resulting expression directly as

$$
\begin{aligned}
\mathcal{T}_*^{\overline{\overline{s}}} :=\ &\frac{\mathrm{D}^{\overline{s}}E^{\overline{\overline{s}}}}{\mathrm{D}t}-\theta^{\overline{\overline{s}}}\frac{\mathrm{D}^{\overline{s}}\eta^{\overline{\overline{s}}}}{\mathrm{D}t}-\sum_{i\in\mathfrak{I}_s}\mu^{\overline{is}}\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{s}}}\rho^s\omega^{i\overline{s}})}{\mathrm{D}t}\\
&-\sum_{\kappa\in\mathfrak{I}_{\mathrm{cs}}}\left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_\kappa-\mathbf{v}_s\right)\sigma_s:\frac{\mathsf{C}_s}{j_s}\right\rangle_{\Omega_\kappa,\Omega}-\sum_{\kappa\in\mathfrak{I}_{\mathrm{cs}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\kappa,\Omega}
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}s}^{-}}\ \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}}\left\langle \mathbf{n}_s\cdot\left(\mathbf{v}_\kappa-\mathbf{v}_s\right)\sigma_s^{*}{:}\frac{\mathsf{C}_s}{j_s}\right\rangle_{\Omega_\kappa,\Omega} \\
&-\frac{1}{2}\sum_{\beta\in\mathfrak{J}_{\mathrm{c}s}^{-}}\ \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\beta}^{-}}\left\langle \mathbf{n}_s\cdot\mathsf{t}_s^{*}\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\kappa,\Omega}+\left\langle \eta_s\frac{\mathrm{D}^{\overline{s}}\left(\theta_s-\theta^{\overline{\overline{s}}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega} \\
&+\sum_{i\in\mathfrak{J}_s}\left\langle \rho_s\omega_{is}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{is}-\mu^{\overline{is}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}-\nabla\cdot\left\langle\left(\mathsf{t}_s-\sigma_s{:}\frac{\mathsf{C}_s}{j_s}\mathsf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega} \\
&-\varepsilon^{\overline{\overline{s}}}\mathsf{t}^{s}{:}\mathbf{d}^{\overline{\overline{s}}}+\varepsilon^{\overline{\overline{s}}}\sigma^{\overline{\overline{s}}}{:}\frac{\mathsf{C}^{s}}{j^{s}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}}+\left\langle\left(\nabla\cdot\mathsf{t}_s-\nabla\sigma_s{:}\frac{\mathsf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}=0\,. \qquad (7.80)
\end{aligned}
$$

7.5.4 *Solid-phase Potential Energy*

The equation for the solid phase entity potential energy can be obtained, based on Eq. (7.79) or on Eq. (7.58) with α replaced by s, as

$$
\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{s}}}:=\frac{\mathrm{D}^{\overline{s}}\Psi^{\overline{\overline{s}}}}{\mathrm{D}t}-\sum_{i\in\mathfrak{J}_s}\psi^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{s}}\left(\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}}\right)}{\mathrm{D}t}-\sum_{i\in\mathfrak{J}_s}\left\langle\rho_s\omega_{is}\frac{\mathrm{D}^{\overline{s}}\psi^{\overline{is}}}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}=0\,. \qquad (7.81)
$$

7.6 Interface Energy Dynamics

The manipulations needed to derive the desired macroscale dynamic equations for an interface are analogous to those performed for fluid phases. The primary difference arises from the fact that microscale interfaces are two-dimensional entities. Thus, when evaluating temporal and spatial derivatives of microscale interface properties, it is important to restrict the time derivative so that it remains fixed to a point on the moving surface; the divergence and gradient operators must be two-dimensional. When the microscale Gibbs-Duhem equation is employed, this dimensionality must be accounted for. The derivatives of macroscale quantities should be formulated so that the resulting expressions are similar to those appearing in the conservation equations. Here we will derive species-based and entity-based dynamic relations that are of greatest utility for the analysis of porous medium systems. We will take advantage of some of the insights gained from the analysis of fluids to expedite the derivations.

7.6.1 Interface Species Energy

The average of the microscale Euler equation for a chemical species in an interface, Eq. (3.189), is provided in Table 7.1. The material derivative of this expression gives the dynamic equation for macroscale internal energy,

$$\frac{\mathrm{D}^{\overline{i\alpha}} E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}} \frac{\mathrm{D}^{\overline{i\alpha}} \eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}})}{\mathrm{D}t} - \eta^{\overline{\overline{i\alpha}}} \frac{\mathrm{D}^{\overline{i\alpha}} \theta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t}$$
$$- \frac{\mathrm{D}^{\overline{i\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \gamma^{\alpha} X^{\overline{\overline{i\alpha}}})}{\mathrm{D}t} - \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} \mu^{\overline{i\alpha}}}{\mathrm{D}t} = 0 \quad \text{for } i \in \Im_s, \alpha \in \Im_{\mathrm{I}} \,. \qquad (7.82)$$

Proceeding as with our analysis of the phase equations, we introduce the averaging operator for the last three terms to obtain

$$\frac{\mathrm{D}^{\overline{i\alpha}} E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}} \frac{\mathrm{D}^{\overline{i\alpha}} \eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}})}{\mathrm{D}t} - \left\langle \eta_{i\alpha} \frac{\mathrm{D}^{\overline{i\alpha}} \theta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega}$$
$$- \frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t} \langle \gamma_\alpha X_{i\alpha} \rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}^{\overline{i\alpha}} \mu^{\overline{i\alpha}}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} = 0 \,. \qquad (7.83)$$

At this point we seek to derive some expressions for substitution into Eq. (7.83). In anticipation of working with the material derivative of the microscale Gibbs-Duhem equation, we define the material derivative operator that acts on a surface,

$$\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t} = \frac{\partial'}{\partial t} + \mathbf{v}^{\overline{s}} \cdot \nabla' \quad \text{for } \mathbf{x} \in \Omega_\alpha, \alpha \in \Im_{\mathrm{I}} \,. \qquad (7.84)$$

This operator is not a macroscale operator in that it distinguishes the surface and evaluates the time and space derivative on that surface. The macroscale velocity, $\mathbf{v}^{\overline{s}}$, is not associated with the surface being examined but merely provides a reference velocity. Making use of the definition of the time derivative provided by Eq. (7.36), we can show that

$$\frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t} = \frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t} + \left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}} \right) \cdot \nabla - \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{I} - \mathbf{I}'_\alpha \right) \cdot \nabla \quad \text{for } \mathbf{x} \in \Omega_\alpha, \alpha \in \Im_{\mathrm{I}} \,. \quad (7.85)$$

This identity can be applied to the material derivatives of $\theta^{\overline{\overline{i\alpha}}}$ and $\mu^{\overline{i\alpha}}$ in Eq. (7.83) so that the equation becomes

$$\frac{\mathrm{D}^{\overline{i\alpha}} E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}} \frac{\mathrm{D}^{\overline{i\alpha}} \eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}})}{\mathrm{D}t} - \left\langle \eta_{i\alpha} \frac{\mathrm{D}'^{\overline{s}} \theta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega}$$
$$- \frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t} \langle \gamma_\alpha X_{i\alpha} \rangle_{\Omega_\alpha,\Omega} - \left\langle \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}'^{\overline{s}} \mu^{\overline{i\alpha}}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega}$$

$$
\begin{aligned}
&-\left[\eta^{\overline{\overline{i\alpha}}}\nabla\theta^{\overline{\overline{i\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{i\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&+\left\langle\eta_{i\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}_{\alpha}'\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\theta^{\overline{\overline{i\alpha}}}\\
&+\left\langle\rho_{\alpha}\omega_{i\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}_{\alpha}'\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\mu^{\overline{i\alpha}}=0\,. \qquad (7.86)
\end{aligned}
$$

To obtain a relation for further development of this equation, we wish to consider the microscale Gibbs-Duhem equation for a surface, Eq. (3.192). Because the quantities in this equation are associated with the surface, temporal and spatial differentials must be calculated on the surface. The operator defined in Eq. (7.84) may be employed to obtain

$$
\eta_{i\alpha}\frac{\mathrm{D}^{\prime\overline{s}}\theta_{\alpha}}{\mathrm{D}t}+X_{i\alpha}\frac{\mathrm{D}^{\prime\overline{s}}\gamma_{\alpha}}{\mathrm{D}t}+\rho_{\alpha}\omega_{i\alpha}\frac{\mathrm{D}^{\prime\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}-\rho_{\alpha}\omega_{i\alpha}\left.\left(\frac{\mathrm{D}^{\prime\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}\right)\right|_{\gamma_{\alpha},\theta_{\alpha}}=0
$$
$$
\text{for } \mathbf{x}\in\Omega_{\alpha},\alpha\in\mathfrak{I}_{\mathrm{I}}\,. \qquad (7.87)
$$

Rearrangement of the second term in this equation, using the product rule followed by application of the averaging operator, $\langle\cdot\rangle_{\Omega_{\alpha},\Omega}$, gives

$$
\begin{aligned}
&\left\langle\eta_{i\alpha}\frac{\mathrm{D}^{\prime\overline{s}}\theta_{\alpha}}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}+\left\langle\frac{\mathrm{D}^{\prime\overline{s}}(\gamma_{\alpha}X_{i\alpha})}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}-\left\langle\gamma_{\alpha}\frac{\mathrm{D}^{\prime\overline{s}}X_{i\alpha}}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}\\
&\quad+\left\langle\rho_{\alpha}\omega_{i\alpha}\frac{\mathrm{D}^{\prime\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}-\left\langle\rho_{\alpha}\omega_{i\alpha}\left.\left(\frac{\mathrm{D}^{\prime\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}\right)\right|_{\gamma_{\alpha},\theta_{\alpha}}\right\rangle_{\Omega_{\alpha},\Omega}=0\,. \qquad (7.88)
\end{aligned}
$$

Addition of Eq. (7.88) to Eq. (7.86) with collection of similar terms then provides the identity

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{i\alpha}}E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t}-\theta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{i\alpha}}\eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t}-\mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}\\
&\quad+\left\langle\eta_{i\alpha}\frac{\mathrm{D}^{\prime\overline{s}}(\theta_{\alpha}-\theta^{\overline{\overline{i\alpha}}})}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}+\left\langle\rho_{\alpha}\omega_{i\alpha}\frac{\mathrm{D}^{\prime\overline{s}}(\mu_{i\alpha}-\mu^{\overline{i\alpha}})}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}\\
&\quad-\frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t}\langle\gamma_{\alpha}X_{i\alpha}\rangle_{\Omega_{\alpha},\Omega}+\left\langle\frac{\mathrm{D}^{\prime\overline{s}}(\gamma_{\alpha}X_{i\alpha})}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}-\left\langle\gamma_{\alpha}\frac{\mathrm{D}^{\prime\overline{s}}X_{i\alpha}}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}\\
&\quad-\left\langle\rho_{\alpha}\omega_{i\alpha}\left.\left(\frac{\mathrm{D}^{\prime\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}\right)\right|_{\gamma_{\alpha},\theta_{\alpha}}\right\rangle_{\Omega_{\alpha},\Omega}\\
&\quad-\left[\eta^{\overline{\overline{i\alpha}}}\nabla\theta^{\overline{\overline{i\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{i\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&\quad+\left\langle\eta_{i\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}_{\alpha}'\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\theta^{\overline{\overline{i\alpha}}}\\
&\quad+\left\langle\rho_{\alpha}\omega_{i\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}_{\alpha}'\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\mu^{\overline{i\alpha}}=0\,. \qquad (7.89)
\end{aligned}
$$

We seek to simplify the combination of the two material derivatives involving $\gamma_\alpha X_{i\alpha}$. This can be done by making use of the averaging theorems. We expand the two material derivatives involving $\gamma_\alpha X_{i\alpha}$ that appear in Eq. (7.89) in terms of time and space derivatives, with $\gamma_\alpha X_{i\alpha}$ replaced by f_α for convenience, such that

$$\begin{aligned}\frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t}\langle f_\alpha\rangle_{\Omega_\alpha,\Omega}-\left\langle\frac{\mathrm{D}'^{\overline{s}}f_\alpha}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}&=\frac{\partial}{\partial t}\langle f_\alpha\rangle_{\Omega_\alpha,\Omega}+\mathbf{v}^{\overline{i\alpha}}\cdot\nabla\langle f_\alpha\rangle_{\Omega_\alpha,\Omega}\\&-\left\langle\frac{\partial' f_\alpha}{\partial t}\right\rangle_{\Omega_\alpha,\Omega}-\mathbf{v}^{\overline{s}}\cdot\left\langle\nabla' f_\alpha\right\rangle_{\Omega_\alpha,\Omega}\,.\end{aligned}\tag{7.90}$$

We refer to Table 6.1 and apply averaging theorem T[2,(3,0),0] to the third term on the right side and theorem G[2,(3,0),0] to the last term. After regrouping the resulting expressions, we obtain

$$\begin{aligned}\frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t}\langle f_\alpha\rangle_{\Omega_\alpha,\Omega}-\left\langle\frac{\mathrm{D}'^{\overline{s}}f_\alpha}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}&=\nabla\cdot\left\langle\mathbf{l}'_\alpha f_\alpha\right\rangle_{\Omega_\alpha,\Omega}\cdot\left(\mathbf{v}^{\overline{i\alpha}}-\mathbf{v}^{\overline{s}}\right)\\&-\nabla\cdot\left\langle\left(\mathbf{l}-\mathbf{l}'_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{i\alpha}}\right)f_\alpha\right\rangle_{\Omega_\alpha,\Omega}-\left\langle\left(\mathbf{l}-\mathbf{l}'_\alpha\right)f_\alpha\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\overline{i\alpha}}}\\&-\left\langle\nabla'\cdot\mathbf{l}'_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)f_\alpha\right\rangle_{\Omega_\alpha,\Omega}+\sum_{\kappa\in\mathfrak{J}^-_{c\alpha}}\left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)f_\alpha\right\rangle_{\Omega_\kappa,\Omega}\\&\qquad\text{for } i\in\mathfrak{J}_s,\alpha\in\mathfrak{J}_\mathrm{I}\,.\end{aligned}\tag{7.91}$$

If f_α in Eq. (7.91) reverts back to $\gamma_\alpha X_{i\alpha}$, the difference on the left side of the equation is what appears in Eq. (7.89). Therefore, application of theorem Eq. (7.91) to the sixth and seventh terms in Eq. (7.89) provides the final expression,

$$\begin{aligned}\mathcal{T}_*^{\overline{\overline{i\alpha}}}:=&\frac{\mathrm{D}^{\overline{i\alpha}}E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t}-\theta^{\overline{\overline{i\alpha}}}\frac{\mathrm{D}^{\overline{i\alpha}}\eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t}-\mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}})}{\mathrm{D}t}\\&-\sum_{\kappa\in\mathfrak{J}^-_{c\alpha}}\left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\kappa,\Omega}\\&+\left\langle\eta_{i\alpha}\frac{\mathrm{D}'^{\overline{s}}(\theta_\alpha-\theta^{\overline{\overline{i\alpha}}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}+\left\langle\rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}'^{\overline{s}}(\mu_{i\alpha}-\mu^{\overline{i\alpha}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}\\&-\left\langle\gamma_\alpha\frac{\mathrm{D}'^{\overline{s}}X_{i\alpha}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}-\left\langle\rho_\alpha\omega_{i\alpha}\left(\frac{\mathrm{D}'^{\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}\right)\Bigg|_{\gamma_\alpha,\theta_\alpha}\right\rangle_{\Omega_\alpha,\Omega}\\&-\left[\eta^{\overline{\overline{i\alpha}}}\nabla\theta^{\overline{\overline{i\alpha}}}+\nabla\cdot\left\langle\mathbf{l}'_\alpha\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\alpha,\Omega}+\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{i\alpha}}-\mathbf{v}^{\overline{s}}\right)\\&+\nabla\cdot\left\langle\left(\mathbf{l}-\mathbf{l}'_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{i\alpha}}\right)\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\alpha,\Omega}+\left\langle\left(\mathbf{l}-\mathbf{l}'_\alpha\right)\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\overline{i\alpha}}}\\&+\left\langle\nabla'\cdot\mathbf{l}'_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\alpha,\Omega}\\&+\left\langle\eta_{i\alpha}\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{i\alpha}}}\end{aligned}$$

$$+\left\langle \rho_\alpha \omega_{i\alpha} \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha\right) \right\rangle_{\Omega_\alpha,\Omega} \cdot \nabla \mu^{\overline{i\alpha}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I}\,. \tag{7.92}$$

7.6.2 Interface Species Potential Energy

The body force potential for a species in an interface can be differentiated, similarly to that for a fluid phase, to obtain

$$\frac{\mathrm{D}^{\overline{i\alpha}} \Psi^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \psi^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}})}{\mathrm{D}t} - \left\langle \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}^{\overline{i\alpha}} \psi^{\overline{i\alpha}}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I}\,, \tag{7.93}$$

where the averaging operator has been introduced. We make use of the identity provided by Eq. (7.85) so that Eq. (7.93) becomes

$$\begin{aligned} &\frac{\mathrm{D}^{\overline{i\alpha}} \Psi^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \psi^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}})}{\mathrm{D}t} - \left\langle \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}'^{\overline{s}} \psi^{\overline{i\alpha}}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} \\ &- \left\langle \rho_\alpha \omega_{i\alpha} \left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right) \cdot \nabla \psi^{\overline{i\alpha}} \right\rangle_{\Omega_\alpha,\Omega} \\ &+ \left\langle \rho_\alpha \omega_{i\alpha} \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha\right) \cdot \nabla \psi^{\overline{i\alpha}} \right\rangle_{\Omega_\alpha,\Omega} = 0\,. \end{aligned} \tag{7.94}$$

After evaluatiing the averaging operator in the next to the last term on the right side and performing minor rearrangement, motivated by the organization of terms in Eq. (7.92), we obtain

$$\begin{aligned} \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}} := &\frac{\mathrm{D}^{\overline{i\alpha}} \Psi^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \psi^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}})}{\mathrm{D}t} - \left\langle \rho_\alpha \omega_{i\alpha} \frac{\mathrm{D}'^{\overline{s}} \psi^{\overline{i\alpha}}}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} \\ &- \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}} \nabla \psi^{\overline{i\alpha}} \cdot \left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right) \\ &+ \left\langle \rho_\alpha \omega_{i\alpha} \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha\right) \right\rangle_{\Omega_\alpha,\Omega} \cdot \nabla \psi^{\overline{i\alpha}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I}_\mathrm{I}\,. \end{aligned} \tag{7.95}$$

7.6.3 Interface-entity Energy

As has been observed in deriving the entity-based expressions of energy dynamics for phases, the needed equation can be obtained formally by manipulating the Euler equation for an entity or by summing the species-based form over all species in the entity. These approaches may be applied to the interface as well, and the steps for producing the desired results parallel those used in deriving the phase-based equations, which are summarized in Table 7.2. A less formal approach is to note the differences between the species-based and entity-based equations for a phase, particularly for a fluid phase, and assume that parallel modifications will occur in developing the interface entity form from Eq. (7.92). Regardless of the method used to obtain it, the entity-based dynamic condition for the energy that results is

$$\begin{aligned}
\mathcal{T}_{*}^{\overline{\overline{\alpha}}} :=\; & \frac{\mathrm{D}^{\overline{\alpha}} E^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{\alpha}}} \frac{\mathrm{D}^{\overline{\alpha}} \eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \sum_{i \in \mathfrak{J}_s} \mu^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}})}{\mathrm{D}t} \\
& - \sum_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^{-}} \left\langle \mathbf{n}_{\alpha} \cdot \left(\mathbf{v}_{\kappa} - \mathbf{v}^{\overline{s}} \right) \gamma_{\alpha} \right\rangle_{\Omega_{\kappa},\Omega} \\
& + \left\langle \eta_{\alpha} \frac{\mathrm{D}'^{\overline{s}} (\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}})}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} + \sum_{i \in \mathfrak{J}_s} \left\langle \rho_{\alpha} \omega_{i\alpha} \frac{\mathrm{D}'^{\overline{s}} (\mu_{i\alpha} - \mu^{\overline{i\alpha}})}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \\
& - \left[\eta^{\overline{\overline{\alpha}}} \nabla \theta^{\overline{\overline{\alpha}}} + \nabla \cdot \left\langle \mathsf{I}'_{\alpha} \gamma_{\alpha} \right\rangle_{\Omega_{\alpha},\Omega} + \sum_{i \in \mathfrak{J}_s} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \nabla \mu^{\overline{i\alpha}} \right] \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right) \\
& + \nabla \cdot \left\langle \left(\mathsf{I} - \mathsf{I}'_{\alpha} \right) \cdot \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{\alpha}} \right) \gamma_{\alpha} \right\rangle_{\Omega_{\alpha},\Omega} + \left\langle \left(\mathsf{I} - \mathsf{I}'_{\alpha} \right) \gamma_{\alpha} \right\rangle_{\Omega_{\alpha},\Omega} : \mathbf{d}^{\overline{\overline{\alpha}}} \\
& + \left\langle \nabla' \cdot \mathsf{I}'_{\alpha} \cdot \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{s}} \right) \gamma_{\alpha} \right\rangle_{\Omega_{\alpha},\Omega} + \left\langle \eta_{\alpha} \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathsf{I} - \mathsf{I}'_{\alpha} \right) \right\rangle_{\Omega_{\alpha},\Omega} \cdot \nabla \theta^{\overline{\overline{\alpha}}} \\
& + \sum_{i \in \mathfrak{J}_s} \left\langle \rho_{\alpha} \omega_{i\alpha} \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathsf{I} - \mathsf{I}'_{\alpha} \right) \right\rangle_{\Omega_{\alpha},\Omega} \cdot \nabla \mu^{\overline{i\alpha}} = 0 \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{I}} \,. \qquad (7.96)
\end{aligned}$$

This equation is provided without a formal proof. It is easily and directly written down based on the results presented for a fluid phase, Eqs. (7.44) and (7.54), extended to predict the notational changes that should be incorporated into Eq. (7.92) to arrive at Eq. (7.96). Listing the steps of the formal derivation is unnecessary.

7.6.4 Interface-entity Potential Energy

As with the internal energy dynamic equation, the dynamic equation for the entity-based energy potential follows directly from the species-based form, Eq. (7.95), and is

$$\begin{aligned}
\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}} :=\; & \frac{\mathrm{D}^{\overline{\alpha}} \Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \sum_{i \in \mathfrak{J}_s} \psi^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{\alpha}} (\varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}})}{\mathrm{D}t} - \sum_{i \in \mathfrak{J}_s} \left\langle \rho_{\alpha} \omega_{i\alpha} \frac{\mathrm{D}'^{\overline{s}} \psi^{\overline{i\alpha}}}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \\
& - \sum_{i \in \mathfrak{J}_s} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \nabla \psi^{\overline{i\alpha}} \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right) \\
& + \sum_{i \in \mathfrak{J}_s} \left\langle \rho_{\alpha} \omega_{i\alpha} \left(\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathsf{I} - \mathsf{I}'_{\alpha} \right) \right\rangle_{\Omega_{\alpha},\Omega} \cdot \nabla \psi^{\overline{i\alpha}} = 0 \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{I}} \,. \qquad (7.97)
\end{aligned}$$

7.7 Common Curve Energy Dynamics

When a porous medium system is composed of two or more fluid phases plus a solid phase, common curves will exist where the three phases meet. Thus, a full representation of the system requires expressions for the common curve energy dynamics. The derivation of the appropriate equations follows directly along the lines for the fluid phase and an interface. However, fortunately, there is no need to repeat the derivations to obtain the final expressions! These can be inferred from the phase and interface results. An independent derivation will confirm the results of this section, which are summarized in Table 7.2.

7.7.1 Common Curve Species Energy

The basis for this equation is a comparison of Eq. (7.44) and Eq. (7.92). Based on a superficial examination of these equations, the latter equation for the interface seems more complex. However, if we make four simple changes, Eq. (7.92) will reduce to to the equation for a phase. First, we replace I'_α with $\mathsf{I}_\alpha = \mathsf{I}$, the unit tensor in space. Second, we replace γ_α with $-p_\alpha$, the corresponding term in the Euler equation. Third, we replace the microscale surface operator ∇' with the spatial operator ∇. Fourth, we remove the "$'$" from the material derivative operator relative to the solid velocity within the averaging operator. With these changes, some terms are zero; and the surface equation is transformed to the phase equation. Based on this similarity, we will presume that a similar notational change can provide the equation for a common curve. We replace I'_α in Eq. (7.92) with I''_α, the unit tensor with non-zero components only involving the tangent to the curve. Also, we will change the sign of the interfacial tension consistent with the sign conventions adopted for curvilineal tension as opposed to surface tension. Additionally, ∇' will be replaced by ∇''; and $\mathrm{D}'^{\overline{s}}/\mathrm{D}t$ will be replaced by $\mathrm{D}''^{\overline{s}}/\mathrm{D}t$, where

$$\frac{\mathrm{D}''^{\overline{s}}}{\mathrm{D}t} = \frac{\partial''}{\partial t} + \mathbf{v}^{\overline{s}} \cdot \nabla'' \,, \tag{7.98}$$

such that

$$\frac{\mathrm{D}^{\overline{i\alpha}}}{\mathrm{D}t} = \frac{\mathrm{D}''^{\overline{s}}}{\mathrm{D}t} + \left(\mathbf{v}^{\overline{i\alpha}} - \mathbf{v}^{\overline{s}}\right) \cdot \nabla - \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}''_\alpha\right) \cdot \nabla \quad \text{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J}_{\mathrm{C}} \,. \tag{7.99}$$

With just these cosmetic changes, the equation that describes the dynamics of the curvilineal energy is obtained as

$$\begin{aligned}
\mathcal{T}_*^{\overline{\overline{i\alpha}}} :=& \frac{\mathrm{D}^{\overline{i\alpha}} E^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \theta^{\overline{\overline{i\alpha}}} \frac{\mathrm{D}^{\overline{i\alpha}} \eta^{\overline{\overline{i\alpha}}}}{\mathrm{D}t} - \mu^{\overline{i\alpha}} \frac{\mathrm{D}^{\overline{i\alpha}} (\epsilon^{\overline{\overline{\alpha}}} \rho^\alpha \omega^{i\overline{\alpha}})}{\mathrm{D}t} \\
&+ \sum_{\kappa \in \mathfrak{J}_{\mathrm{c}\alpha}^{-}} \left\langle \mathbf{n}_\alpha \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}}\right) \gamma_\alpha X_{i\alpha} \right\rangle_{\Omega_\kappa, \Omega}
\end{aligned}$$

$$
\begin{aligned}
&+\left\langle \eta_{i\alpha}\frac{\mathrm{D}''^{\overline{s}}(\theta_\alpha-\theta^{\overline{\overline{i\alpha}}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}+\left\langle \rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}''^{\overline{s}}(\mu_{i\alpha}-\mu^{\overline{i\alpha}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}\\
&+\left\langle \gamma_\alpha\frac{\mathrm{D}''^{\overline{s}}X_{i\alpha}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}-\left\langle \rho_\alpha\omega_{i\alpha}\left(\frac{\mathrm{D}''^{\overline{s}}\mu_{i\alpha}}{\mathrm{D}t}\right)\Bigg|_{\gamma_\alpha,\theta_\alpha}\right\rangle_{\Omega_\alpha,\Omega}\\
&-\left[\eta^{\overline{\overline{i\alpha}}}\nabla\theta^{\overline{\overline{i\alpha}}}-\nabla\cdot\left\langle\mathbf{l}''_\alpha\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\alpha,\Omega}+\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{i\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&-\nabla\cdot\left\langle\left(\mathbf{l}-\mathbf{l}''_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{i\alpha}}\right)\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\alpha,\Omega}-\left\langle\left(\mathbf{l}-\mathbf{l}''_\alpha\right)\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\overline{i\alpha}}}\\
&-\left\langle\nabla''\cdot\mathbf{l}''_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha X_{i\alpha}\right\rangle_{\Omega_\alpha,\Omega}\\
&+\left\langle\eta_{i\alpha}\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{i\alpha}}}\\
&+\left\langle\rho_\alpha\omega_{i\alpha}\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\mu^{\overline{i\alpha}}=0\quad\text{for } i\in\mathfrak{I}_s,\alpha\in\mathfrak{I}_{\mathrm{C}}\,.\qquad(7.100)
\end{aligned}
$$

If desired, a rigorous derivation, starting with the macroscale Euler equation for a curve in Table 7.1, can be undertaken to confirm Eq. (7.100).

7.7.2 *Common Curve Species Potential Energy*

The equation for the energy potential of a chemical species in a common curve may be obtained from Eq. (7.95) for a species in an interface by making notational changes as just described such that

$$
\begin{aligned}
\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}}:=&\frac{\mathrm{D}^{\overline{i\alpha}}\Psi^{\overline{\overline{i\alpha}}}}{\mathrm{D}t}-\psi^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{i\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}})}{\mathrm{D}t}-\left\langle\rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}''^{\overline{s}}\psi^{\overline{i\alpha}}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}\\
&-\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\nabla\psi^{\overline{i\alpha}}\cdot\left(\mathbf{v}^{\overline{i\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&+\left\langle\rho_\alpha\omega_{i\alpha}\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\psi^{\overline{i\alpha}}=0\quad\text{for } i\in\mathfrak{I}_s,\alpha\in\mathfrak{I}_{\mathrm{C}}\,.\qquad(7.101)
\end{aligned}
$$

7.7.3 *Common Curve Entity Energy*

For the common curve entity as a whole, the dynamic equation for energy may be obtained by making notational alterations as described in Sect. 7.7.1 to Eq. (7.96). Alternatively, one can sum the species equation over all species or perform the derivation starting with the Euler equation. In all instances, the result is

$$
\mathcal{T}_{*}^{\overline{\overline{\alpha}}}:=\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\sum_{i\in\mathfrak{I}_s}\mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}})}{\mathrm{D}t}
$$

$$
\begin{aligned}
&+\sum_{\kappa\in\mathfrak{J}_{c\alpha}^{-}} \left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha\right\rangle_{\Omega_\kappa,\Omega} \\
&+\left\langle \eta_\alpha \frac{\mathrm{D}''^{\overline{s}}(\theta_\alpha-\theta^{\overline{\overline{\alpha}}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} + \sum_{i\in\mathfrak{J}_s}\left\langle \rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}''^{\overline{s}}(\mu_{i\alpha}-\mu^{\overline{i\alpha}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} \\
&-\left[\eta^{\overline{\overline{\alpha}}}\nabla\theta^{\overline{\overline{\alpha}}}-\nabla\cdot\left\langle \mathbf{I}''_\alpha\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}+\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\nabla\mu^{\overline{i\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right) \\
&-\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}''_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}-\left\langle\left(\mathbf{I}-\mathbf{I}''_\alpha\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\alpha}} \\
&-\left\langle\nabla''\cdot\mathbf{I}''_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega} \\
&+\left\langle\eta_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}} \\
&+\sum_{i\in\mathfrak{J}_s}\left\langle\rho_\alpha\omega_{i\alpha}\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\mu^{\overline{i\alpha}}=0 \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{C}}\,. \qquad (7.102)
\end{aligned}
$$

7.7.4 *Common Curve Entity Potential Energy*

The dynamics of the common curve energy potential are described, following the processes described previously based on the species-based form, Eq. (7.101), as

$$
\begin{aligned}
\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}} := {}& \frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\sum_{i\in\mathfrak{J}_s}\psi^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}})}{\mathrm{D}t}-\sum_{i\in\mathfrak{J}_s}\left\langle\rho_\alpha\omega_{i\alpha}\frac{\mathrm{D}''^{\overline{s}}\psi^{\overline{i\alpha}}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega} \\
&-\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\omega^{i\overline{\alpha}}\nabla\psi^{\overline{i\alpha}}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right) \\
&+\sum_{i\in\mathfrak{J}_s}\left\langle\rho_\alpha\omega_{i\alpha}\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\psi^{\overline{i\alpha}}=0 \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{C}}\,. \qquad (7.103)
\end{aligned}
$$

The final equations for the common curves are designated in Table 7.2 for easy reference. The entity-based equations, in particular, will be used in subsequent chapters; the species-based forms are included for completeness and for use in more complex analyses.

7.8 Equilibrium Conditions

The final objective of this chapter is to determine a set of macroscale equilibrium conditions. These conditions are important, because they are used to guide the formulation of closure relations for TCAT models based on the entropy inequality. Here we will consider the equilibrium conditions that must hold for single-fluid-phase and two-fluid-phase porous medium systems. The conditions for the single-fluid-phase case must hold for the two-fluid-phase case, but additional conditions must also apply for the latter case. These systems are considered here because they will be analyzed in more detail in subsequent chapters. For both cases, the equilibrium conditions are obtained as averages of the microscale conditions determined by variational analysis in Chap. 4.

7.8.1 Two-phase Equilibrium Conditions

The macroscale equilibrium conditions for a single-fluid-phase porous medium system should be in terms of macroscale averages and variables that appear in the macroscale conservation, balance, and thermodynamic equations. They should also be consistent with the microscale conditions derived in Sect. 4.5. Although microscale equilibrium conditions can be averaged in an infinite variety of ways, we will employ averaging operators that lead to macroscale quantities that are defined to be equivalent to quantities that appear in the dynamic macroscopic equations.

For the case of single-fluid-phase flow in a porous medium, the index set is

$$\mathcal{I} = \{w, s, ws\} \,, \tag{7.104}$$

where w refers to the fluid phase, s to the solid phase, and ws to the interface between these phases. The equilibrium condition for microscale temperature, given as Eq. (4.49), is

$$\theta_w = \theta_s = \theta_{ws} = \lambda_{\mathbb{S}} \,, \tag{7.105}$$

where $\lambda_{\mathbb{S}}$ is a constant. Since microscale temperature is constant at equilibrium and equal in all entities, an average temperature defined as $\langle \theta_\alpha \rangle_{\Omega_\alpha,\Omega_\alpha,W}$ will equal the microscale temperature at equilibrium regardless of the weighting function employed. In our development of the Euler forms of the macroscale thermodynamic relations, we made use of entropy density as the weighting function. Thus, for consistency, we will use this same weighting function such that we have the species-based equilibrium condition on temperature,

$$\theta^{\overline{\overline{i\alpha}}} = \langle \theta_\alpha \rangle_{\Omega_\alpha,\Omega_\alpha,\eta_{i\alpha}} = \lambda_{\mathbb{S}} \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I} \,. \tag{7.106}$$

For the entity-based temperatures, we have the equilibrium condition

$$\theta^{\overline{\overline{\alpha}}} = \langle \theta_\alpha \rangle_{\Omega_\alpha,\Omega_\alpha,\eta_\alpha} = \lambda_{\mathbb{S}} \quad \text{for } \alpha \in \mathcal{I} \,. \tag{7.107}$$

It is important to recognize that both of these conditions express the fact that the macroscale temperature is constant at equilibrium and equal to the constant microscale equilibrium temperature. The importance of the weighting function comes into play if one is interested in near-equilibrium system conditions. If a temperature variation exists in a system, the macroscale temperature we have defined will not necessarily be equal to the intrinsic average temperature, the geometric average temperature, or any other average. Consider the case of a closed, isolated system in which the temperature is not uniform but the heat capacity is constant. For the sake of discussion, also assume that changes in density and pressure can be ignored. A temperature averaged over this system, weighted with respect to the heat capacity, would be time invariant as the system relaxed to equilibrium. However, if entropy, or any function that depends on temperature, is used as the weighting function for averaging, the average temperature will exhibit a time dependence. Alternatively, if the average temperature is calculated as the inverse of the average inverse temperature, it will exhibit time dependence as the system relaxes to equilibrium. We note that the macroscale condition of equilibrium is somewhat less stringent than the microscale condition, in that subscale processes are not explicitly accounted for. However, the weighting with respect to entropy minimizes this problem and also ensures consistency between microscale and macroscale CIT thermodynamic formalisms.

Another macroscale equilibrium condition on temperature involves the average temperature of an entity at its boundary. For the two-phase case, this can be expressed as

$$\langle \theta_w \rangle_{\Omega_{ws},\Omega_{ws},\eta_w} = \langle \theta_s \rangle_{\Omega_{ws},\Omega_{ws},\eta_s} = \langle \theta_{ws} \rangle_{\Omega_{ws},\Omega_{ws},\eta_{ws}} = \lambda_{\mathbb{S}} \tag{7.108}$$

or

$$\theta_w^{\overline{\overline{ws}}} = \theta_s^{\overline{\overline{ws}}} = \theta^{\overline{\overline{ws}}} = \lambda_{\mathbb{S}} \, . \tag{7.109}$$

This condition obviously holds at equilibrium because the temperature is uniform and constant. Additionally, this condition will be useful in many cases where the microscale temperature is continuous at the *ws* interface in the direction normal to the interface. When this microscale condition holds, Eq. (7.109) may be only approximate if the system is not at equilibrium because the weighting functions employed to calculate the average temperatures are different for each entity.

A similar averaging approach to obtain equilibrium conditions can be applied to terms involving potentials, where the microscale condition given by Eq. (4.50) is

$$\mu_{iw} + \psi_{iw} = \mu_{is} + \psi_{is} + \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3\rho_s j_s} = \mu_{iws} + \psi_{iws} = \lambda_{\mathbb{M}_i} \quad \text{for } i \in \mathfrak{J}_s \, . \tag{7.110}$$

Because $\lambda_{\mathbb{M}_i}$ is a constant, each of the groups of terms in the equality must also be a constant at equilibrium. Therefore, each item can be averaged with a different weighting function without destroying the equality. We will use $\rho_\alpha \omega_{i\alpha}$ for each species i in entity α so that we obtain mass weighted averages. The resulting macroscale equilibrium condition is

$$\mu^{\overline{iw}} + \psi^{\overline{iw}} = \mu^{\overline{is}} + \psi^{\overline{is}} + \left\langle \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3\rho_s j_s} \right\rangle_{\Omega_s,\Omega_s,\rho_s\omega_{is}} = \mu^{\overline{iws}} + \psi^{\overline{iws}} = \lambda_{\mathbb{M}_i} \quad \text{for } i \in \mathfrak{J}_s \, . \tag{7.111}$$

When the distribution of chemical species i in the solid is uniform such that it does not impact the evaluation of the solid stress terms in the averaging operator, the average may be calculated with

$$\mu^{\overline{iw}} + \psi^{\overline{iw}} = \mu^{\overline{is}} + \psi^{\overline{is}} + \frac{\sigma^{\overline{\overline{s}}}:\mathbf{C}^s}{3\rho^s j^s} = \mu^{\overline{iws}} + \psi^{\overline{iws}} = \lambda_{\mathbb{M}_i}, \quad \text{for } i \in \mathcal{J}_s \,. \tag{7.112}$$

The three microscale equilibrium conditions related to solid phase stress as given in Eqs. (4.51)–(4.54) can also be averaged over their appropriate domains. The condition within the solid phase, which was noted to be redundant with the equilibrium condition from the momentum equation, is written simply as an average with

$$\left\langle \nabla\cdot\mathbf{t}_s - \rho_s \nabla\left(\frac{\mathbf{t}_s:\mathbf{I}}{3\rho_s}\right)\right\rangle_{\Omega_s,\Omega_s} = \mathbf{0} \,. \tag{7.113}$$

The equilibrium condition for the normal forces acting on the ws interface is obtained as an average of Eq. (4.52) over the interface so that

$$\langle p_w + \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - (\nabla\cdot\mathbf{n}_w)\,\gamma_{ws} + \rho_{ws}\mathbf{n}_w\cdot\mathbf{g}_{ws}\rangle_{\Omega_{ws},\Omega_{ws}} = 0 \,. \tag{7.114}$$

After evaluation of the averaging notation as possible, this result is expressed as

$$p_w^{ws} + (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)_s^{ws} - \left\langle(\nabla'\cdot\mathbf{n}_w)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega_{ws}} + \rho^{ws}\left(\mathbf{g}_{ws}\cdot\mathbf{n}_w\right)^{\overline{ws}} = 0 \,. \tag{7.115}$$

The equilibrium condition on the tangential stress at the surface of the solid phase is obtained from Eq. (4.54). Averaging this equation over the ws interface within the averaging volume yields

$$\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'\right\rangle_{\Omega_{ws},\Omega_{ws}} = \mathbf{0} \,. \tag{7.116}$$

The second term in this equation is a phase average over the ws interface of a property of the solid that relies on the orientation of the interface.

It is somewhat unsatisfying to leave parts of these conditions in terms of the averaging operator rather than identifying unique averages that can be carried forward. However, there is no guidance available as to how to define the averages so that the definitions will be consistent across various equations. Therefore, decisions about definitions of averages of some variables, such as an average of $\nabla'\cdot\mathbf{n}_w$, and the use of approximations in making definitions are postponed until the definitions are needed in facilitating closure of the model.

7.8.2 Three-phase Equilibrium Conditions

The second case to be considered is the macroscale equilibrium conditions that hold for a two-fluid-phase porous medium system consisting of the seven entities with the index set

$$\mathcal{J} = \{w, n, s, wn, ws, ns, wns\} \ . \tag{7.117}$$

We use w and n as indices to denote the fluid phases; s is the index for the solid phase; wn, ws, and ns are the indices for the interfaces; and wns is the common curve index. We will make use of index sets that are subsets of $\mathcal{J}$ designated as follows:

$$\text{fluid phases:} \qquad \mathcal{J}_{\mathrm{f}} = \{w, n\} \ ; \tag{7.118}$$

$$\text{all phases:} \qquad \mathcal{J}_{\mathrm{P}} = \{w, n, s\} \ ; \tag{7.119}$$

$$\text{all interfaces:} \qquad \mathcal{J}_{\mathrm{I}} = \{wn, ws, ns\} \ ; \tag{7.120}$$

$$\text{common curve:} \qquad \mathcal{J}_{\mathrm{C}} = \{wns\} \ ; \tag{7.121}$$

and

$$\text{all entities except the solid:} \qquad \mathcal{J}_{/S} = \{w, n, wn, ws, ns, wns\} \ . \tag{7.122}$$

As with the single-fluid-phase case, the microscale equilibrium conditions can be averaged over entity domains to the macroscale in a form that is consistent with the definitions of the macroscale variables that have already been employed.

The microscale temperatures are equal and constant at equilibrium, based on Eq. (4.61). Therefore, the macroscale temperatures will also be equal, even if computed using different weighting functions. Similarly to the two-phase case, the condition on the temperatures based on averaging with the species-based entropy of the entity is

$$\theta^{\overline{\overline{i\alpha}}} = \langle \theta_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha, \eta_{i\alpha}} = \lambda_{\mathbb{S}} \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J} \ . \tag{7.123}$$

If the thermodynamic formulation considers the entity as a whole, the macroscale temperature is obtained using the entropy density as the weighting function such that

$$\theta^{\overline{\overline{\alpha}}} = \langle \theta_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha, \eta_\alpha} = \lambda_{\mathbb{S}} \quad \text{for } \alpha \in \mathcal{J} \ . \tag{7.124}$$

These conditions state that the macroscale temperatures of all species and entities will be equal at equilibrium.

A set of equilibrium conditions for the microscale potentials is given by Eq. (4.62). Averaging this condition using the mass density of the chemical species as the weighting function provides the macroscale thermodynamic equilibrium conditions

$$\mu^{\overline{i\alpha}} + \psi^{\overline{i\alpha}} = \lambda_{\mathbb{M}_i} \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_{/S} \tag{7.125}$$

and

$$\mu^{\overline{is}} + \psi^{\overline{is}} + \left\langle \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{3\rho_s j_s} \right\rangle_{\Omega_s, \Omega_s, \rho_s \omega_{is}} = \lambda_{\mathbb{M}_i} \quad \text{for } i \in \mathcal{J}_s \ . \tag{7.126}$$

At equilibrium, these sums of macroscale chemical and body force potentials, along with an additional term for an elastic solid, will be equal to each other and constant. Disequilibrium in these variables produces, primarily, a driving force for flow, transport, and chemical reactions.

For the two-fluid-phase case, Eq. (4.63) was obtained as the microscale equilibrium condition within the solid. This condition is identical to that for the single fluid and provides the macroscale equilibrium condition identical to Eq. (7.113) given as

$$\left\langle \nabla\cdot\mathbf{t}_s - \rho_s \nabla\left(\frac{\mathbf{t}_s:\mathbf{I}}{3\rho_s}\right)\right\rangle_{\Omega_s,\Omega_s} = \mathbf{0} \, . \tag{7.127}$$

The conditions on the surface for the tangential solid stress are obtained from Eq. (4.99) as

$$\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_\alpha \right\rangle_{\Omega_\alpha,\Omega_\alpha} = \mathbf{0} \qquad \text{for } \alpha\in\{ws,ns\} \, , \tag{7.128}$$

and from Eq. (4.101) as

$$\left\langle \mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{l}''_{wns} \right\rangle_{\Omega_{wns},\Omega_{wns}} = 0 \, . \tag{7.129}$$

The equilibrium balances of normal forces on the three interfaces are also stated as averages of microscale conditions at the interfaces. From Eq. (4.91) at the *wn* interface we obtain

$$\left\langle p_w - p_n + \rho_{wn}\mathbf{g}_{wn}\cdot\mathbf{n}_w - (\nabla'\cdot\mathbf{n}_w)\gamma_{wn} \right\rangle_{\Omega_{wn},\Omega_{wn}} = 0 \, , \tag{7.130}$$

which may also be expressed in terms of macroscale variables as

$$p_w^{wn} - p_n^{wn} + \rho^{wn}\left(\mathbf{g}_{wn}\cdot\mathbf{n}_w\right)^{\overline{wn}} - \left\langle (\nabla'\cdot\mathbf{n}_w)\gamma_{wn} \right\rangle_{\Omega_{wn},\Omega_{wn}} = 0 \, . \tag{7.131}$$

In Eq. (7.131), the averaging notation has been employed for the first three terms, while the last term has been left in terms of the averaging operator because unique notation will have to be introduced to eliminate the operator later in the analysis of a macroscale system.

The microscale conditions at the fluid solid interfaces, *ws* and *ns*, were derived as Eqs. (4.94) and (4.95), respectively. Averaging of these relations over their corresponding interfaces and introduction of the averaging notation gives

$$p_w^{ws} + \left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\right)_s^{ws} + \rho^{ws}\left(\mathbf{g}_{ws}\cdot\mathbf{n}_w\right)^{\overline{ws}} - \left\langle (\nabla'\cdot\mathbf{n}_w)\gamma_{ws} \right\rangle_{\Omega_{ws},\Omega_{ws}} = 0 \tag{7.132}$$

and

$$p_n^{ns} + \left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\right)_s^{ns} + \rho^{ns}\left(\mathbf{g}_{ns}\cdot\mathbf{n}_n\right)^{\overline{ns}} - \left\langle (\nabla'\cdot\mathbf{n}_n)\gamma_{ns} \right\rangle_{\Omega_{ns},\Omega_{ns}} = 0 \, . \tag{7.133}$$

Two additional microscale conditions of equilibrium have been derived for the common curve and are provided as Eqs. (4.103) and (4.104). The former describes the balance of forces tangent to the solid surface acting normal to the common curve while the latter provides the equilibrium balance of forces at the common curve normal to the solid surface. Each of these conditions is averaged over the common curve to obtain the macroscale equilibrium conditions

$$\left\langle \gamma_{wn}\cos\varphi_{ws,wn} \right\rangle_{\Omega_{wns},\Omega_{wns}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} - \rho^{wns}\left(\mathbf{g}_{wns}\cdot\mathbf{n}_{ws}\right)^{\overline{wns}}$$

$$+\left\langle \gamma_{wns}\kappa_{Gwns}\right\rangle_{\Omega_{wns},\Omega_{wns}}=0 \tag{7.134}$$

and

$$-\left\langle \gamma_{wn}\sin\varphi_{ws,wn}\right\rangle_{\Omega_{wns},\Omega_{wns}}-\rho^{wns}\left(\mathbf{g}_{wns}\cdot\mathbf{n}_s\right)^{\overline{wns}}+\left\langle \gamma_{wns}\kappa_{Nwns}\right\rangle_{\Omega_{wns},\Omega_{wns}} \\ +\left(\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s\right)^{wns}=0\,. \tag{7.135}$$

Unique averages will have to be defined to eliminate the averaging operator from these last two equations.

7.9 Summary

In this chapter, we have formulated macroscale thermodynamic equations based on microscale CIT. The microscale equations were averaged to obtain macroscale Euler and Gibbs-Duhem expressions for chemical species and for fluid, elastic solid, interface, and common curve entities. The macroscale Euler equations, along with the equation numbers of their microscale precursors in Chap. 3, are listed in Table 7.1. Based on these equations, dynamic energy equations were derived for the internal energy and the body force potential energy. The equations were put into forms that will prove to be particularly convenient when analyzing porous medium systems. The results are spread throughout the chapter, so Table 7.2 has been provided for easy location of the important final relations. These thermodynamic equations provide the means to relate terms that appear in the entropy balance to terms that appear in the conservation equations.

Macroscale equilibrium conditions were derived by averaging the microscale equilibrium conditions to the macroscale. The equilibrium conditions developed will guide the arrangement of the entropy inequality, constrained by conservation equations, into a form that facilitates the postulation of closure relations needed to complete the TCAT models.

Exercises

7.1. Derive Eq. (7.13) by averaging Eq. (3.156).

7.2. Prove Eq. (7.55) is satisfied by summing Eq. (7.44) over $\mathcal{I}_s$ to obtain Eq. (7.54).

7.3. Derive Eq. (7.80) by starting with the material derivative of the Euler equation for a solid phase entity, as found in Table 7.1.

7.4. Derive the identity given as Eq. (7.85).

7.5. Derive Eq. (7.97) starting with the microscale condition

$$\Psi_\alpha = \sum_{i\in\mathfrak{I}_s} \rho_\alpha \omega_{i\alpha} \psi_{i\alpha} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I} \,.$$

7.6. Derive Eq. (7.100) by starting with the macroscale Euler equation for a species on a common curve as given in Table 7.1.

7.7. Derive the macroscale equilibrium total normal stress on the solid surface, $\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Gamma_s,\Gamma_s}$, for a two-fluid-phase system.

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Chapter 8
Evolution Equations

8.1 Overview

The goal of this chapter is to formulate macroscale evolution equations for geometric densities that can be applied to complete the formulation of closed, solvable TCAT models. These densities are quantities such as the amount of volume per averaging volume occupied by a phase or the amount of area between phases per volume occupied by an interface between phases. The need for the evolution equations for geometric properties is rooted in the fact that these quantities do not exist at the microscale but arise in the averaging process. The evolution of these properties is based on system kinematics rather than conservation equations; and the evolution equations are extracted from averaging theorems, as depicted by the TCAT framework elements in Fig. 8.1.

Recall that in formulating TCAT models we seek an entropy inequality (EI) that is in the form of products of independent sets of fluxes and forces. These products describe entropy production resulting from dissipative processes. Guidance for structuring the EI into force-flux form is provided, in part, by equilibrium conditions as terms are grouped together. The grouping process also encounters quantities that are the geometric densities. Although the material derivatives of these quantities are zero at equilibrium, they are not independent conditions as are needed in formulation of force-flux products. For example, a change in volume fraction of a phase is not independent of the area bounding the phase. The simplest example of this fact is a spherical bubble that expands in space. While its volume changes, its surface area must also change with the only independent variable being the radius. Of course for porous media systems the relations between changing volumes and areas will be far more complex. The relation among the geometric quantities and their evolution cannot be deduced from either conservation equations or thermodynamic relations. The relations among changes in geometric densities are based on differential geometry considerations. Although some formulations have claimed that evolution of geometric density can be ascertained from conservation equations [e.g., 10–12], these models are not generally useful. Relations among geometric entities and equations

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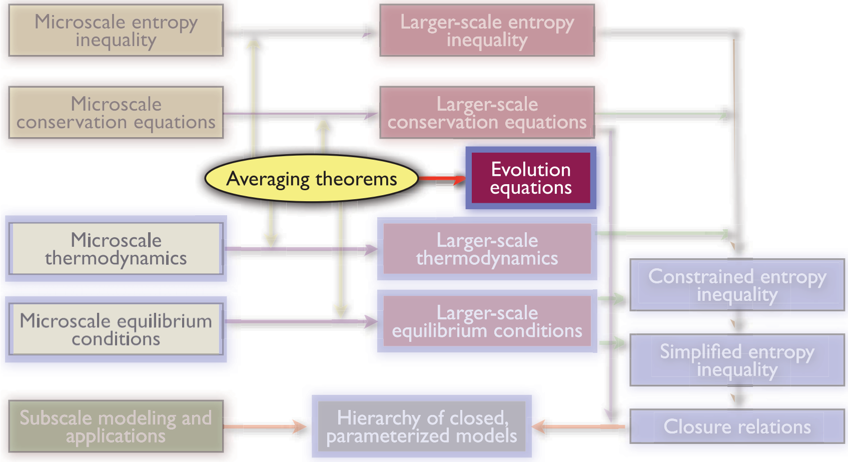

Fig. 8.1 TCAT elements of interest in Chapter 8 for derivation of the kinematic evolution equations (after [5])

for their evolution are independent of system physics as described by conservation and thermodynamic equations. This fact has been recognized, for example, in considering the interface between water and ice [1] and between bubbles and a flowing fluid in the absence of a solid [6, 8]. Some relatively simple efforts at accounting for interface evolution for porous media have appeared [2, 7].

In developing evolution equations for geometric densities, one should be aware of two important features. First, interfaces and common curves may be massless. When an interface is massless, the interface mass conservation equation reduces to a jump condition between phases. Similarly, all terms containing density will drop out of the momentum equation for a massless entity such that the momentum equation provides information only as jump conditions. When an interface is not massless, it may have momentum. In that instance, velocities of mass within the interface can be determined from the momentum equation. However, driving forces for flow within an interface are different from those that cause movement of the interface itself in a direction normal to the surface. Similar comments apply to a common curve.

These observations lead to the second important point relating to movements that cause a change in geometric density. A volume fraction will change only as a result of the normal velocity of the boundary of the phase of interest. Tangential velocities of the boundary or of fluid within the boundary do not impact the volume fraction. If there is mass within the boundary of the phase (i.e., for the case of an interface containing mass), the velocity of the mass normal to the interface is the normal velocity of the interface. However, the presence of mass within the interface is not required for an interface to exist and move. Somewhat differently, the geometric density of an interface can change due to the normal velocity of a curve that forms the boundary of the interface but also due to changes in the shape of the interface, even if its boundary is fixed or non-existent (as with a closed surface). Again, movement tangent to the surface of the interface or tangent to the common curve bounding the interface does not alter interface density. Common curve densities change due to movement of the points at the end of the common curve and due to deformation of the curve. We emphasize that these movements are not velocities of material and impact the geometric density identically whether or not the entity contains mass. We will expect, then, that equations for evolution of the geometric densities will contain only normal velocities to the entities. The macroscale averages of these velocities are not directly obtainable from macroscale averages of material velocities that also account for tangential movement.

Based upon the above considerations, a need exists to relate geometric quantities in multiphase porous medium systems and to approximate interface and common curve velocities under a general set of conditions. The averaging theorems, which are mathematical relations independent of conservation principles, will be used as bases for evolution equations. We will also apply these relations to the special cases of single-fluid-phase and two-fluid-phase porous medium systems to provide some approximate evolution equations that will be useful in the EI.

8.2 Derivation of Evolution Equations

Evolution equations are needed for quantities such as the porosity, volume fractions, fluid saturations, specific interfacial areas, and specific common curve densities. Because these quantities are inter-related in porous media, some systematic procedure is needed to develop these equations. Although it is not possible to obtain exact macroscale equations for all cases based on differential geometry [9], the averaging theorems provide forms that can serve as a basis for obtaining good approximations.

8.2.1 General Expression

To obtain the general expressions, we begin with the averaging theorems as found in Table 6.1. In particular, we will use the "T" and "G" theorems without the singularities or concentrated functions. These terms, which appear in the $[3,(3,0),0]$ family of theorems, account for direct transfer of a property between a phase and a common curve. Here this will be unimportant as the function being averaged is smooth. For convenience, rather than developing the expressions for phases, interfaces, and common curves separately, we will make use of general forms of the theorems.

From Table 6.1, it can be seen that the theorem $\mathrm{T}(3-n,(3,0),0)$ can be expressed as

$$\left\langle \frac{\partial^{(n)} f_\alpha}{\partial t} \right\rangle_{\Omega_\alpha,\Omega} = \frac{\partial}{\partial t}\langle f_\alpha \rangle_{\Omega_\alpha,\Omega} + \nabla\cdot\left\langle \left(\mathbf{I}-\mathbf{I}_\alpha^{(n)}\right)\cdot\mathbf{v}_\alpha f_\alpha \right\rangle_{\Omega_\alpha,\Omega}$$

$$+\left\langle \nabla^{(n)}\cdot\mathbf{I}_{\alpha}^{(n)}\cdot\mathbf{v}_{\alpha}f_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} - \sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}^{-}} \langle \mathbf{n}_{\alpha}\cdot\mathbf{v}_{\kappa}f_{\alpha}\rangle_{\Omega_{\kappa},\Omega} \quad \text{for } \alpha\in\mathcal{J}\,, \tag{8.1}$$

where $3-n$ is the dimensionality of the domain and (n) indicates the number of primes that appear. Similarly, the gradient theorems $\mathrm{G}(3-n,(3,0),0)$ for the various entities are written, based on the expressions in Table 6.1, as

$$\begin{aligned}\left\langle \nabla^{(n)}f_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} &= \nabla\langle f_{\alpha}\rangle_{\Omega_{\alpha},\Omega} - \nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}_{\alpha}^{(n)}\right)f_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\\ &\quad -\left\langle \nabla^{(n)}\cdot\mathbf{I}_{\alpha}^{(n)}f_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} + \sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}^{-}} \langle \mathbf{n}_{\alpha}f_{\alpha}\rangle_{\Omega_{\kappa},\Omega} \quad \text{for } \alpha\in\mathcal{J}\,. \end{aligned}\tag{8.2}$$

To obtain expressions for geometric entities, we examine the theorems for the special case when $f_{\alpha}=1$. The left sides of Eqs. (8.1) and (8.2) both become zero, and the first terms on the right can be expressed in terms of average values based on the definition of specific entity measures given by Eq. (6.9). Equations (8.1) and (8.2) become, respectively,

$$\begin{aligned}\frac{\partial\epsilon^{\overline{\overline{\alpha}}}}{\partial t} &+ \nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}_{\alpha}^{(n)}\right)\cdot\mathbf{v}_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega} + \left\langle \nabla^{(n)}\cdot\mathbf{I}_{\alpha}^{(n)}\cdot\mathbf{v}_{\alpha}\right\rangle_{\Omega_{\alpha},\Omega}\\ &- \sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}^{-}} \langle \mathbf{n}_{\alpha}\cdot\mathbf{v}_{\kappa}\rangle_{\Omega_{\kappa},\Omega} = 0 \quad \text{for } \alpha\in\mathcal{J} \end{aligned}\tag{8.3}$$

and

$$\begin{aligned}\nabla\epsilon^{\overline{\overline{\alpha}}} &- \nabla\cdot\left\langle\mathbf{I}-\mathbf{I}_{\alpha}^{(n)}\right\rangle_{\Omega_{\alpha},\Omega} - \left\langle \nabla^{(n)}\cdot\mathbf{I}_{\alpha}^{(n)}\right\rangle_{\Omega_{\alpha},\Omega}\\ &+ \sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}^{-}} \langle \mathbf{n}_{\alpha}\rangle_{\Omega_{\kappa},\Omega} = 0 \quad \text{for } \alpha\in\mathcal{J}\,. \end{aligned}\tag{8.4}$$

These last two equations may be combined to obtain a material derivative form by taking the dot product of Eq. (8.4) with any macroscale velocity and adding it to Eq. (8.3). In our exploitation of the entropy inequality, we make use of velocities referenced to the solid-phase velocity, $\mathbf{v}^{\overline{s}}$. Therefore, without any approximation or loss of generality, we will use $\mathbf{v}^{\overline{s}}$ as the macroscale velocity. We note, also, that a macroscale velocity may be moved inside the averaging operator. Taking the dot product of $\mathbf{v}^{\overline{s}}$ with Eq. (8.4) and adding the result to Eq. (8.3) then gives

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + \nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}_{\alpha}^{(n)}\right)\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{\alpha},\Omega} + \left\langle\mathbf{I}-\mathbf{I}_{\alpha}^{(n)}\right\rangle_{\Omega_{\alpha},\Omega}:\mathbf{d}^{\overline{\overline{s}}}\\ &+\left\langle \nabla^{(n)}\cdot\mathbf{I}_{\alpha}^{(n)}\cdot\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{\alpha},\Omega} - \sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}^{-}} \left\langle \mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{\kappa},\Omega} = 0 \quad \text{for } \alpha\in\mathcal{J}\,. \end{aligned}\tag{8.5}$$

Based on this exact (within the scale considerations of the averaging theorems) expression, we will now consider approximations and simplifications that apply to single-fluid-phase and two-fluid-phase flow in a porous medium system. The simplifications allow us to relate changes in volume fractions, interfacial area densities, and common curve length densities.

8.3 Single-fluid-phase Flow

For single-fluid-phase flow in a porous medium, $\mathcal{J} = \{w, s, ws\}$. We will apply Eq. (8.5) to each of the three entities and then examine interactions among the three evolution equations obtained.

8.3.1 *Phases*

For the solid phase $\alpha = s$, $\nabla^{(n)} = \nabla$, and $\mathsf{I}_{\alpha}^{(n)} = \mathsf{I}$. The lower order connected set, $\mathcal{J}_{\mathrm{cs}}^{-}$, is *ws*. With these identifications, Eq. (8.5) becomes

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} - \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} = 0\,. \tag{8.6}$$

This equation indicates that the rate of change of $\varepsilon^{\overline{\overline{s}}}$ is due to the normal movement of the boundary of the solid phase. When the evaluation of the quantity in the averaging operator is positive, the solid-phase volume fraction is increasing. Recall also that

$$\varepsilon^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{w}}} = 1 \tag{8.7}$$

for a single-fluid-phase porous medium system. Thus, the rates of change of the volume fractions of the two phases are directly related with

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} + \frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} = 0\,. \tag{8.8}$$

Therefore, Eq. (8.6) may alternatively be written

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} - \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} = 0\,, \tag{8.9}$$

where use has been made of the fact that $\mathbf{n}_s = -\mathbf{n}_w$ on Ω_{ws}. Equation (8.9) may alternatively be obtained directly from Eq. (8.5).

Equation (8.8) is an immediately useful equation because it contains only macroscopic dependent variables. On the other hand, either Eq. (8.6) or Eq. (8.9) can be employed only with difficulty because each contains the microscale variable $\mathbf{v}_{ws}$ and the microscale normal to the interface. Exact evaluation of the average indicated is not generally possible. However, we can examine the evolution equation for the interface and attempt to arrive at a reasonable approximation.

8.3.2 Interface

For the interface in single-fluid-phase porous media flow, $\alpha = ws$, $\nabla^{(n)} = \nabla'$, and $\mathsf{I}_{\alpha}^{(n)} = \mathsf{I} - \mathbf{n}_s\mathbf{n}_s = \mathsf{I} - \mathbf{n}_w\mathbf{n}_w$. Because there is no common curve, the lower order connected set, $\mathcal{J}_{\mathrm{cws}}^{-}$, is the empty set. For this case, Eq. (8.5) reduces to

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{ws}}}}{\mathrm{D}t} + \nabla\cdot\left\langle \mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} + \left\langle \mathbf{n}_s\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}:\mathbf{d}^{\overline{\overline{s}}}$$
$$- \left\langle \left(\nabla'\cdot\mathbf{n}_s\right)\mathbf{n}_s\cdot\left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} = 0 \,. \tag{8.10}$$

This equation is more difficult to deal with than the equation for the phase. Nevertheless if we make use of some understanding of the physics of the system, we can obtain a useful approximate kinematic equation.

8.4 Single-fluid-phase Flow Geometric Relations

A cornerstone of the approximations to be examined here is the fact that solid-phase kinematics are much slower than fluid-phase kinematics. Within an averaging volume, the solid phase moves slowly, and variations of microscale solid-phase velocities around $\mathbf{v}^{\overline{s}}$ can be considered small. With these approximations invoked, we will write an evolution approximation for the solid-phase behavior. For the sake of generality, this approximation will be written in the context of multiple fluid phases.

Evolution Approximation 8.1 (Solid Behavior)
The solid is considered to behave such that the following approximations hold:

- *the deformation, curvature, and orientation of the solid-phase surface in the normal direction is independent of the fluid phases wetting the surface;*
- *the mass-averaged velocity of the solid phase is essentially equivalent to the surface-averaged velocity of the solid phase over all fractions of the surface independent of the fluid wetting the surface;*
- *the curvature of the solid surface is uncorrelated with the difference between the normal component of the velocity of fluid-solid interfaces and the component of the macroscale velocity of the solid phase in that direction; and*
- *the orientation of the solid surface is uncorrelated with the velocity of the surface.*

To make use of this approximation, let us first consider the microscale surface orientation tensor for the solid phase in this system, defined as

$$\mathsf{G}_{ws} := \mathsf{I} - \mathsf{I}'_{ws} = \mathbf{n}_s\mathbf{n}_s = \mathbf{n}_w\mathbf{n}_w \quad \text{for } \mathbf{x} \in \Omega_{ws} \,. \tag{8.11}$$

This tensor is related to the orientation of the normal direction of the ws interface. With reference to Eq. (8.10), the microscale orientation tensor appears within an averaging operator, so we define the macroscale surface orientation tensor, which is also of interest, as

$$\mathsf{G}^{\alpha} = \left\langle \mathsf{I} - \mathsf{I}'_{\alpha} \right\rangle_{\Omega_\alpha,\Omega_\alpha} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{I}} \, . \tag{8.12}$$

Therefore, for the *ws* interface in the single-fluid-phase system,

$$\mathsf{G}^{ws} = \left\langle \mathsf{I} - \mathsf{I}'_{ws} \right\rangle_{\Omega_{ws},\Omega_{ws}} = \left\langle \mathbf{n}_w \mathbf{n}_w \right\rangle_{\Omega_{ws},\Omega_{ws}} = \left\langle \mathbf{n}_s \mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega_{ws}} \, . \tag{8.13}$$

The macroscale tensor G^{ws} is a measure of the average orientation of the surface of the *s* phase. G^{ws} is a symmetric tensor with $\mathrm{tr}\,\mathsf{G}^{ws} = 1$. For a solid whose surface is isotropic in that it has no dominant normal direction, $\mathsf{G}^{ws} = \mathsf{I}/3$. Note that G^{ws} is a quantity that is computable from knowledge of the microscale phase morphology. This quantity will change if the mean orientation of the phase distribution changes. For example, physical intuition suggests that for a typical slightly compressible or incompressible solid phase in a porous medium system, the solid-phase surface orientation will change slowly.

The microscale tensor G_{ws} appears in the second and third terms of Eq. (8.10) within the averaging operator. In the second term, it multiplies a velocity difference; but in the third term it appears by itself. When the terms within an averaging operator are not correlated, the average of the product can be written as the product of averages. If the terms are only approximately uncorrelated, splitting the product will be an approximation.

Here we will consider that the second term can be approximated by breaking the product that appears within the averaging operator. This assumption is based on the fourth bullet of Evolution Approximation 8.1 that the orientation of the solid surface is not correlated to its movement. With this assumption

$$\nabla\cdot \left\langle \mathbf{n}_s \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{ws},\Omega} \approx \nabla\cdot \left[\mathsf{G}^{ws} \cdot \left(\mathbf{v}^{ws} - \mathbf{v}^{\bar{s}} \right) \varepsilon^{\overline{\overline{ws}}} \right] . \tag{8.14}$$

By the assumption that the average of the surface velocity is approximately equal to the average velocity of the solid phase, this divergence term can be considered negligibly small. Thus, Eq. (8.10) reduces, after evaluation of the average in the third term, to

$$\frac{\mathrm{D}^{\bar{s}} \varepsilon^{\overline{\overline{ws}}}}{\mathrm{D}t} + \varepsilon^{\overline{\overline{ws}}} \mathsf{G}^{ws} {:} \mathbf{d}^{\bar{\bar{s}}} - \left\langle \left(\nabla' \cdot \mathbf{n}_s \right) \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{ws},\Omega} = 0 \, . \tag{8.15}$$

Next, consider the microscale surface property denoted by the quantity $\nabla' \cdot \mathbf{n}_s$. This is a scalar measure of the change in the normal direction of the *ws* surface due to a change in location on the surface. This quantity is the curvature of the surface and is denoted as J_s where

$$J_s = \nabla' \cdot \mathbf{n}_s \quad \text{for } \mathbf{x} \in \Gamma_s \, . \tag{8.16}$$

The macroscale curvature of a surface, J_s^{ws}, results from averaging over the interface and is defined as

$$J_s^{ws} := \left\langle \nabla' \cdot \mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega_{ws}} . \tag{8.17}$$

It is worth noting that we can also define J_w^{ws} as

$$J_w^{ws} = -J_s^{ws} = \left\langle \nabla' \cdot \mathbf{n}_w \right\rangle_{\Omega_{ws},\Omega_{ws}} . \tag{8.18}$$

If we invoke the solid-phase evolution approximation that the curvature of the solid surface is not correlated to the relative velocity of the *ws* interface, Eq. (8.15) becomes

$$\frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{ws}}}}{\mathrm{D}t} + \varepsilon^{\overline{\overline{ws}}} \mathsf{G}^{ws} {:} \mathbf{d}^{\overline{\overline{s}}} - J_s^{ws} \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} = 0 . \tag{8.19}$$

To obtain an equation that is written completely in terms of macroscale properties, we can eliminate the averaging operator term by substituting in Eq. (8.6) and rearranging the order of terms, yielding

$$\frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{ws}}}}{\mathrm{D}t} - J_s^{ws} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} + \varepsilon^{\overline{\overline{ws}}} \mathsf{G}^{ws} {:} \mathbf{d}^{\overline{\overline{s}}} = 0 . \tag{8.20}$$

For a porous medium, J_s^{ws} is positive. Equation (8.20) expresses the change in interfacial area between the solid and fluid phases (i.e., the surface area of the solid) due to a change in volume fraction of the solid associated with microscale rearrangement of phase morphology and to compression of the solid within the averaging volume. We emphasize that this is an approximate equation that can be tested in the context of a real system. Because the assumptions included in this approximation have been stated explicitly, we can re-examine them should this equation prove to be inadequate for a single-phase system of interest. The geometric orientation tensor, G^{ws}, and the curvature of the *ws* interface, J_s^{ws}, are important physical quantities in porous medium systems. These quantities account macroscopically for some elements of interface morphology. The dynamic behavior of these properties may change from system to system and will influence the system behavior.

In conclusion, we note that the relations that will be useful in modeling the geometric evolution of the *w*, *s*, and *ws* entities in single-fluid-phase flow are the identity Eq. (8.7) and the approximate relation Eq. (8.20), which are based on averaging theorems and Evolution Approximation 8.1. Neither of these relations is based on conservation principles so that they are additional independent mathematical conditions that supplement the fundamental relations based on physical processes.

8.5 Two-fluid-phase Flow

In comparison to single-fluid-phase flow, the equations for evolution of macroscopic measures of the distribution of material within a system consisting of two fluid phases plus a solid are more difficult to obtain. For this system, the set of entities is $\mathfrak{I} = \{w,n,s,wn,ws,ns,wns\}$, an increase from three to seven entities in comparison to the single-fluid-phase case. In the single-phase case, all changes in the distribution of $\varepsilon^{\overline{\overline{w}}}$ and $\varepsilon^{\overline{\overline{ws}}}$ can be expressed in terms of the solid-phase distribution, which changes very slowly, if at all. By comparison, the two-fluid-phase case involves movement and redistribution of the w and n fluid phases as well as their boundaries. These redistributions occur at the same time scale as fluid velocities and thus impact the system behavior at much smaller time scales than does solid movement. Approximations of the type employed for the solid behavior as listed in Evolution Approximation 8.1 do not apply to the fluid phases. The equations that we will develop are more prone to significant error because the approximations used in their development are less robust. Although the need for evolution equations is not open to debate, the postulation of appropriate equations requires careful thought and must be subjected to experimental validation. Here we postulate reasonable first-order descriptions based on the averaging theorems.

8.5.1 Solid Phase

In light of the first bulleted item in Evolution Approximation 8.1 for the solid phase, that the solid-phase behavior is independent of the fluid phases wetting the surface, we expect that an equation similar to Eq. (8.15) will be obtained to describe the relation between the total solid surface and the solid-phase volume fraction. An equation obtained should reduce to this form when the two-fluid-phase case reduces to the single-fluid situation. Thus, our derivation will keep this fact in mind.

For the solid phase, $\alpha = s$, $\nabla^{(n)} = \nabla$ and $\mathbf{I}_{\alpha}^{(n)} = \mathbf{I}$ in the general evolution expression, Eq. (8.5). The lower order connected set is $\mathcal{J}_{\mathrm{cs}}^{-} = \{ws, ns\}$. Therefore the solid-phase evolution equation is written

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} - \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} - \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ns} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ns},\Omega} = 0 \,. \tag{8.21}$$

This equation is virtually the same as Eq. (8.6) in that the rate of change of solid-phase volume fraction is related to integration over the solid surface.

It is helpful to decouple the dependence of the change in $\varepsilon^{\overline{\overline{s}}}$ so that it can be expressed in terms of the movement of the ws and ns interfaces independently. The approximations to accomplish this are physically motivated and the reasonableness of the approximations can be evaluated if detail at the microscale is available. The approximations will be denoted formally to highlight their importance and to provide an entry point for re-examination of the solid-phase evolution equation formulation if the equation produced is found to be insufficiently accurate.

Evolution Approximation 8.1 states that the deformation of the solid phase surface is not correlated to the fluid with which the solid is in contact. With this assumption, the fraction of the change in $\varepsilon^{\overline{\overline{s}}}$ associated with the movement of a particular fluid phase can be attributed to the fraction of the surface that is in contact with that phase. Thus, we decompose Eq. (8.21) into parts associated with each fluid and write the approximation

$$\chi_s^{\overline{\overline{\kappa}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}-\left\langle \mathbf{n}_s\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\kappa,\Omega}=0 \quad \text{for } \kappa\in\mathfrak{I}_{\mathrm{cs}}^{-}\,, \tag{8.22}$$

where, in general,

$$\chi_\alpha^{\overline{\overline{\kappa}}}=\langle 1\rangle_{\Omega_\kappa,\Gamma_\alpha} \quad \text{for } \alpha\in\mathfrak{I}, \kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}\,. \tag{8.23}$$

We see that $\chi_s^{\overline{\overline{\kappa}}}$ is the fraction of the solid surface that is wet by the fluid phase that forms the κ interface with the solid. The wetted fraction satisfies the identity

$$\sum_{\kappa\in\mathfrak{I}_{\mathrm{cs}}^{-}}\chi_s^{\overline{\overline{\kappa}}}=1\,. \tag{8.24}$$

Introduction and knowledge of the wetted fraction allows the evolution of $\varepsilon^{\overline{\overline{s}}}$ to be reduced to a dependence of the motion of only a single interface for non-vanishing values of $\chi_s^{\overline{\overline{\kappa}}}$, as given in Eq. (8.22). This is a simplification in comparison to Eq. (8.21), which recognizes that evolution of $\varepsilon^{\overline{\overline{s}}}$ depends on all the fluid phases in contact with the solid. This simplification seems reasonable for many systems and rests on the expectation that the value of $\chi_s^{\overline{\overline{\kappa}}}$ can be estimated based upon the values of other system variables. We reiterate that the validity of these assumptions is subject to experimental study.

8.5.2 Fluid Phases

When $\alpha\in\mathfrak{I}_{\mathrm{f}}$, Eq. (8.5) simplifies similarly to a solid phase to

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{-}}\left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\kappa,\Omega}=0 \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{f}}\,. \tag{8.25}$$

For the case of two fluids, there are two interfaces in $\mathfrak{I}_{\mathrm{c}\alpha}^{-}$. One is the fluid-fluid interface, wn, and the other is the fluid-solid interface, which can be denoted as the αs interface for fluid α. Expansion of the summation in Eq. (8.25) then provides

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_{\alpha s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{\alpha s},\Omega}-\left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}=0 \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{f}}\,. \tag{8.26}$$

Recognizing that $\mathbf{n}_s=-\mathbf{n}_\alpha$ on the αs interface between the fluid and solid, we can substitute Eq. (8.22) into Eq. (8.26) to yield

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\chi_s^{\overline{\overline{\alpha s}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}-\left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}=0 \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{f}}\,. \tag{8.27}$$

The remaining term in the averaging operator in this equation has to do with the dynamics of the fluid-fluid interface. Transformation of this expression to one in terms of macroscale variables is postponed until after the discussion of the *wn* interface and *wns* common curve evolution equations. Equation (8.27) is based on no assumptions other than those relating to the solid phase as listed in Evolution Approximation 8.1.

8.5.3 Fluid-solid Interfaces

Because the dynamics of fluid-solid interfaces are much slower than those of fluid-fluid interfaces, we will treat these two different types separately. The general form of Eq. (8.5) can be particularized to describe the fluid-solid interface behavior. For these interfaces $\alpha \in \mathcal{J}^-_{\mathrm{cs}}$, where for the two-fluid-phase system $\mathcal{J}^-_{\mathrm{cs}} = \{ws, ns\}$. The superscript (n) in the equation is replaced by a single prime, $'$, for an interface. The lower order connected set, $\mathcal{J}^-_{c\alpha}$, consists of the common curve, *wns*. Thus, the interface evolution equation is

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + \nabla\cdot\left\langle\left(\mathsf{I}-\mathsf{I}'_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\alpha,\Omega} + \left\langle\mathsf{I}-\mathsf{I}'_\alpha\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\overline{s}}} + \left\langle\nabla'\cdot\mathsf{I}'_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\alpha,\Omega}$$
$$- \left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0 \quad \text{for } \alpha\in\mathcal{J}^-_{\mathrm{cs}}\,. \tag{8.28}$$

The identities

$$\mathsf{I}-\mathsf{I}'_\alpha = \mathbf{n}_s\mathbf{n}_s \qquad \text{for } \alpha\in\mathcal{J}^-_{\mathrm{cs}}, \mathbf{x}\in\Omega_\alpha \tag{8.29}$$

and

$$\nabla'\cdot\mathsf{I}'_\alpha = -\mathbf{n}_s\nabla'\cdot\mathbf{n}_s \qquad \text{for } \alpha\in\mathcal{J}^-_{\mathrm{cs}}, \mathbf{x}\in\Omega_\alpha \tag{8.30}$$

are invoked to re-express Eq. (8.28) as

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + \nabla\cdot\left\langle\mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\alpha,\Omega} + \left\langle\mathbf{n}_s\mathbf{n}_s\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\overline{s}}} - \left\langle(\nabla'\cdot\mathbf{n}_s)\mathbf{n}_s\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\alpha,\Omega}$$
$$- \left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0 \quad \text{for } \alpha\in\mathcal{J}^-_{\mathrm{cs}}\,. \tag{8.31}$$

We can employ the definition of the macroscale orientation tensor for a surface given by Eq. (8.12). The approximation of Eq. (8.14) may be applied to the second term in Eq. (8.31), followed by the consideration that the resultant term is negligibly small since the solid and its surface have small and nearly equal average velocities. The condition that the curvature of the solid surface, $\nabla'\cdot\mathbf{n}_s$, is not correlated to the normal velocity difference based on Evolution Approximation 8.1 allows the product involving this curvature to be split. With these assumptions, we obtain

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + \varepsilon^{\overline{\overline{\alpha}}}\mathbf{G}^\alpha:\mathbf{d}^{\overline{\overline{s}}} - J^\alpha_s\left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\alpha,\Omega} - \left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0$$

$$\text{for } \alpha \in \mathcal{J}_{\text{cs}}^{-} . \tag{8.32}$$

As a last simplification to be performed in this subsection, we note that Eq. (8.22) can be used to replace the first term in Eq. (8.32) that explicitly involves the averaging operator. After making this substitution, the result is

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t} + \varepsilon^{\overline{\overline{\alpha}}}\mathbf{G}^{\alpha}{:}\mathbf{d}^{\overline{\overline{s}}} - J_s^{\alpha}\chi_s^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} - \left\langle \mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0 \quad \text{for } \alpha \in \mathcal{J}_{\text{cs}}^{-} . \tag{8.33}$$

The material derivative of the specific interfacial area between a solid and fluid is thus shown to depend on a product involving the dilatation of the solid phase, the curvature of the interface multiplying the rate of change of solid volume fraction, and the motion of the common curve bounding the interface in the direction tangent to the surface and normal to the common curve. One consequence of these observations is that only the normal component of the velocity of the interface, and not tangential components within the interface, affects the specific interfacial area. The remaining term involving averaging over the common curve that forms the boundary of the interface will be dealt with subsequently in conjunction with the analysis of the common curve. In the absence of a common curve, such that the α interface is the complete solid surface, Eq. (8.33) reduces to Eq. (8.20) obtained for single-fluid-phase flow.

8.5.4 Fluid-fluid Interface

Equation (8.5) can be employed to describe the dynamics of a fluid-fluid interface. For the two-fluid-phase problem, $\alpha = wn$ corresponds to the fluid-fluid interface. The form of the evolution equation obtained is

$$\begin{aligned}
&\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t} + \nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}'_{wn}\right)\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega} + \left\langle\mathbf{I}-\mathbf{I}'_{wn}\right\rangle_{\Omega_{wn},\Omega}{:}\mathbf{d}^{\overline{\overline{s}}} \\
&+ \left\langle\nabla'\cdot\mathbf{I}'_{wn}\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega} - \left\langle\mathbf{n}_{wn}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0 .
\end{aligned} \tag{8.34}$$

To assist in expressing the quantities in this equation in terms of macroscopic variables, we first note that the orientation tensor, $\mathbf{G}_{wn}$, is defined as

$$\mathbf{G}_{wn} := \mathbf{I} - \mathbf{I}'_{wn} = \mathbf{n}_w\mathbf{n}_w = \mathbf{n}_n\mathbf{n}_n \quad \text{for } \mathbf{x} \in \Omega_{wn} . \tag{8.35}$$

Secondly, the surface divergence of the surface unit tensor is given as

$$\nabla'\cdot\mathbf{I}'_{wn} = -\mathbf{n}_w\nabla'\cdot\mathbf{n}_w = -\mathbf{n}_n\nabla'\cdot\mathbf{n}_n \quad \text{for } \mathbf{x} \in \Omega_{wn} . \tag{8.36}$$

Substitution of these definitions into Eq. (8.34) provides

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t}+\nabla\cdot\left\langle\mathsf{G}_{wn}\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}+\left\langle\mathsf{G}_{wn}\right\rangle_{\Omega_{wn},\Omega}:\mathbf{d}^{\overline{\overline{s}}}\\&\qquad-\left\langle(\nabla'\cdot\mathbf{n}_w)\mathbf{n}_w\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}-\left\langle\mathbf{n}_{wn}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}=0\,.\end{aligned}\tag{8.37}$$

The quantity $\mathsf{G}_{wn}\cdot\mathbf{v}_{wn}$ is the microscale velocity vector of the *wn* interface in the direction normal to the interface. It thus accounts for the important elements of the spatial movement of the interface in changing its shape and size as well as in changing the relative volumes of the adjacent fluid phases. This velocity is defined as $\mathbf{w}_{wn}$ with

$$\mathbf{w}_{wn}:=\mathsf{G}_{wn}\cdot\mathbf{v}_{wn}=\mathbf{n}_w\mathbf{n}_w\cdot\mathbf{v}_{wn}=\mathbf{n}_n\mathbf{n}_n\cdot\mathbf{v}_{wn}\quad\text{for }\mathbf{x}\in\Omega_{wn}\,.\tag{8.38}$$

Substitution of this definition into Eq. (8.37) and evaluation of the first two averaging operator terms yields

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t}+\nabla\cdot\left[\varepsilon^{\overline{\overline{wn}}}\left(\mathbf{w}^{wn}-\mathsf{G}^{wn}\cdot\mathbf{v}^{\overline{s}}\right)\right]+\varepsilon^{\overline{\overline{wn}}}\mathsf{G}^{wn}:\mathbf{d}^{\overline{\overline{s}}}\\&\qquad-\left\langle(\nabla'\cdot\mathbf{n}_w)\mathbf{n}_w\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}-\left\langle\mathbf{n}_{wn}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}=0\,.\end{aligned}\tag{8.39}$$

The quantity $\nabla'\cdot\mathbf{n}_w$ that appears in this equation is the microscale interface curvature, J_w. Rather than decoupling it from the other quantities within the averaging operator at this point, we note that

$$\nabla'\cdot\mathbf{n}_w=J_w^{wn}+(J_w-J_w^{wn})\quad\text{for }\mathbf{x}\in\Omega_{wn}\,.\tag{8.40}$$

Additionally, as was previously developed in Eq. (4.83), for a smooth solid surface, the unit vector $\mathbf{n}_{wn}$ at the common curve can be expressed in terms of the tangent and normal to the solid surface as

$$\mathbf{n}_{wn}=\cos\varphi_{ws,wn}\mathbf{n}_{ws}-\sin\varphi_{ws,wn}\mathbf{n}_s\quad\text{for }\mathbf{x}\in\Omega_{wns}\,,\tag{8.41}$$

where we recall that $\varphi_{ws,wn}$ is the contact angle between the *ws* and *wn* interfaces. Substitution of these last two identities into Eq. (8.39) provides

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t}+\nabla\cdot\left[\varepsilon^{\overline{\overline{wn}}}\left(\mathbf{w}^{wn}-\mathsf{G}^{wn}\cdot\mathbf{v}^{\overline{s}}\right)\right]+\varepsilon^{\overline{\overline{wn}}}\mathsf{G}^{wn}:\mathbf{d}^{\overline{\overline{s}}}\\&\qquad-J_w^{wn}\left\langle\mathbf{n}_w\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}-\left\langle(J_w-J_w^{wn})\mathbf{n}_w\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega}\\&\qquad-\left\langle\cos\varphi_{ws,wn}\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}\\&\qquad+\left\langle\sin\varphi_{ws,wn}\mathbf{n}_s\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}=0\,.\end{aligned}\tag{8.42}$$

The averaging operation premultiplied by J_w^{wn} can be eliminated in favor of macroscale variables by making use of Eq. (8.27) with $\alpha=w$ to obtain

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t}+\nabla\cdot\left[\varepsilon^{\overline{\overline{wn}}}\left(\mathbf{w}^{wn}-\mathsf{G}^{wn}\cdot\mathbf{v}^{\overline{s}}\right)\right]+\varepsilon^{\overline{\overline{wn}}}\mathsf{G}^{wn}:\mathbf{d}^{\overline{\overline{s}}}$$

$$
\begin{aligned}
& - J_w^{wn} \left(\frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} + \chi_s^{\overline{\overline{ws}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} \right) - \left\langle (J_w - J_w^{wn}) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \\
& - \left\langle \cos \varphi_{ws,wn} \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega} \\
& + \left\langle \sin \varphi_{ws,wn} \mathbf{n}_s \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega} = 0 \, . \qquad (8.43)
\end{aligned}
$$

The term involving the difference between the microscale and macroscale interfacial curvatures of the fluid-fluid interface multiplying a velocity difference now must be considered. For the *ws* and *ns* interfaces, we assumed this term was negligible. Such an assumption will not be applicable for the *wn* interface because fluid-fluid interfaces move, deform, and relax to an equilibrium state in response to changes in fluid pressures. These dynamics will, in general, be fast compared to changes in the velocity or the curvature of the solid phase, but slow compared to the rate of propagation of a pressure front. The curvature deviation term from Eq. (8.43) can be written as the macroscale variable $e^{\overline{\overline{wn}}}$, defined as

$$
e^{\overline{\overline{wn}}} := \left\langle (J_w - J_w^{wn}) \, \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \, . \qquad (8.44)
$$

As its curvature changes, so too does the extent of the interface. The measure of this extent is the specific interfacial area. Thus $e^{\overline{\overline{wn}}}$ accounts for the rate of *wn* interfacial area generation as this interface relaxes to an equilibrium state. We substitute Eq. (8.44) into Eq. (8.43), for subsequent additional consideration, to obtain

$$
\begin{aligned}
& \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t} + \nabla \cdot \left[\varepsilon^{\overline{\overline{wn}}} \left(\mathbf{w}^{wn} - \mathbf{G}^{wn} \cdot \mathbf{v}^{\overline{s}} \right) \right] + \varepsilon^{\overline{\overline{wn}}} \mathbf{G}^{wn} : \mathbf{d}^{\overline{\overline{s}}} \\
& \quad - J_w^{wn} \left(\frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} + \chi_s^{\overline{\overline{ws}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} \right) - e^{\overline{\overline{wn}}} - \left\langle \cos \varphi_{ws,wn} \mathbf{n}_{ws} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega} \\
& \quad + \left\langle \sin \varphi_{ws,wn} \mathbf{n}_s \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega} = 0 \, . \qquad (8.45)
\end{aligned}
$$

This equation provides the expression for the change in *wn* interfacial area due to its own deformation as well as to interactions of the interface with the adjacent phases and at the common curve on the solid surface. The last three terms on the left side of Eq. (8.45) need to be expressed in terms of macroscale variables for the equation to be useful in macroscale analysis. Taking this step requires that relations involving the common curve be available that will inform the approximations to be employed. For the moment, we turn to finding an expression that defines the evolution of the *wns* common curve.

8.5.5 Common Curve

Equation (8.5) can be applied to the common curve of the two-fluid-phase system by letting $\alpha = wns$, replacing $(n) = (2)$ by $//$, and observing that $\mathcal{J}^{-}_{\mathrm{cwns}}$ is the null set for this system since there are no common points. Thus the evolution equation for the common curve is

$$\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{wns}}}}{\mathrm{D}t} + \nabla\cdot\left\langle\left(\mathsf{I}-\mathsf{I}''_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} + \left\langle\mathsf{I}-\mathsf{I}''_{wns}\right\rangle_{\Omega_{wns},\Omega}:\mathbf{d}^{\overline{\overline{s}}} \\ + \left\langle\nabla''\cdot\mathsf{I}''_{wns}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0\,. \tag{8.46}$$

For the common curve, we define the orientation tensor G_{wns} as

$$\mathsf{G}_{wns} := \mathsf{I}-\mathsf{I}''_{wns} = \mathsf{I}-\mathbf{l}_{wns}\mathbf{l}_{wns} = \mathbf{n}_s\mathbf{n}_s+\mathbf{n}_{ws}\mathbf{n}_{ws} \quad \text{for } \mathbf{x}\in\Omega_{wns}\,, \tag{8.47}$$

such that it equals the unit tensor minus the dyad of the unit tensors with non-zero components tangent to the curve. Additionally, we know that

$$\nabla''\cdot\mathsf{I}''_{wns} = \mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns} \quad \text{for } \mathbf{x}\in\Omega_{wns}\,. \tag{8.48}$$

Equation (4.87) provides the relation between $\mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns}$ and the normal and geodesic curvatures of the *wns* common line, κ_{Nwns} and κ_{Gwns}, respectively, as

$$\mathbf{l}_{wns}\cdot\nabla''\mathbf{l}_{wns} = \kappa_{Nwns}\mathbf{n}_s+\kappa_{Gwns}\mathbf{n}_{ws} \quad \text{for } \mathbf{x}\in\Omega_{wns}\,. \tag{8.49}$$

Substitution of Eqs. (8.47) and (8.49) into Eq. (8.46) yields

$$\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{wns}}}}{\mathrm{D}t} + \nabla\cdot\left\langle\mathsf{G}_{wns}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} + \left\langle\mathsf{G}_{wns}\right\rangle_{\Omega_{wns},\Omega}:\mathbf{d}^{\overline{\overline{s}}} \\ + \left\langle\kappa_{Nwns}\mathbf{n}_s\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} + \left\langle\kappa_{Gwns}\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0\,. \tag{8.50}$$

We define the velocity of the common curve with components normal to the curve as $\mathbf{w}_{wns}$ with

$$\mathbf{w}_{wns} := \mathsf{G}_{wns}\cdot\mathbf{v}_{wns}\,. \tag{8.51}$$

We also note that

$$\kappa_{Nwns} = \kappa_N^{wns}+\left(\kappa_{Nwns}-\kappa_N^{wns}\right)\,, \tag{8.52}$$

and

$$\kappa_{Gwns} = \kappa_G^{wns}+\left(\kappa_{Gwns}-\kappa_G^{wns}\right)\,. \tag{8.53}$$

Substituting these identities into Eq. (8.50) and evaluating the averaging operations as possible provides

$$\frac{\mathrm{D}^{\overline{s}}\epsilon^{\overline{\overline{wns}}}}{\mathrm{D}t} + \nabla\cdot\left[\epsilon^{\overline{\overline{wns}}}\left(\mathbf{w}^{wns}-\mathsf{G}^{wns}\cdot\mathbf{v}^{\overline{s}}\right)\right] + \epsilon^{\overline{\overline{wns}}}\mathsf{G}^{wns}:\mathbf{d}^{\overline{\overline{s}}} \\ + \kappa_N^{wns}\left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} + \kappa_G^{wns}\left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} \\ + \left\langle\left(\kappa_{Nwns}-\kappa_N^{wns}\right)\mathbf{n}_s\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} \\ + \left\langle\left(\kappa_{Gwns}-\kappa_G^{wns}\right)\mathbf{n}_{ws}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0\,. \tag{8.54}$$

The deviation terms for the normal and geodesic curvature, $e_N^{\overline{\overline{wns}}}$ and $e_G^{\overline{\overline{wns}}}$, may now be defined as

$$e_N^{\overline{\overline{wns}}} := \left\langle (\kappa_{Nwns} - \kappa_N^{wns})\mathbf{n}_s \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{wns},\Omega} \tag{8.55}$$

and

$$e_G^{\overline{\overline{wns}}} := \left\langle (\kappa_{Gwns} - \kappa_G^{wns})\mathbf{n}_{ws} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{wns},\Omega} . \tag{8.56}$$

These terms account for generation of common curve length as the curve relaxes to its equilibrium shape, analogous to $e^{\overline{\overline{wn}}}$ for the fluid-fluid interface defined in Eq. (8.44). Substitution into Eq. (8.54) yields

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wns}}}}{\mathrm{D}t} + \nabla\cdot \left[\varepsilon^{\overline{\overline{wns}}} \left(\mathbf{w}^{wns} - \mathsf{G}^{wns}\cdot\mathbf{v}^{\overline{s}}\right)\right] + \varepsilon^{\overline{\overline{wns}}}\mathsf{G}^{wns}{:}\mathbf{d}^{\overline{\overline{s}}} + \kappa_N^{wns}\left\langle \mathbf{n}_s\cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}$$
$$+ \kappa_G^{wns}\left\langle \mathbf{n}_{ws}\cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} + e_N^{\overline{\overline{wns}}} + e_G^{\overline{\overline{wns}}} = 0 . \tag{8.57}$$

We note that for a system in which the orientation of the common curves is random, $\mathsf{G}^{wns} = 2\mathsf{I}/3$. To evaluate the remaining terms involving the averaging operator in Eq. (8.57), some assumptions will have to be made about the system behavior.

At this point, to complete the derivation of all the expressions involving evolution of geometric densities, evolution approximations applicable to the two-fluid-phase system are needed. We now turn to this task.

8.6 Two-fluid-phase Flow Geometric Relations

In the preceding section, efforts to obtain evolution equations for the fluid-fluid interface and common curve came up against the need to evaluate averaging operators involving integration over these entities. To complete the derivations, evolution approximations in addition to Evolution Approximation 8.1 are required. It has been shown [4] that three independent dynamic relations among entities can be obtained for the two-fluid-phase system. In this section, approximations are employed that facilitate derivation of these relations, which are subsequently used in deriving closure conditions.

8.6.1 Solid Phase and Fluid-solid Interfaces

According to Evolution Approximation 8.1, the behavior of the solid is independent of the fluids with which it is in contact. In Eq. (8.20), the references to the *ws* interface accounts for the total boundary of the solid phase. When two fluid phases are present, we can replace these by the properties of the *ws* and *ns* interfaces that combine as properties of the entire solid boundary.

Perhaps the easiest way to obtain the required equation is based on Eq. (8.33). We can write this equation for $\alpha = ws$ and for $\alpha = ns$. However, for a smooth solid surface, $\mathbf{n}_{ws} = -\mathbf{n}_{ns}$ at the *wns* common curve. Addition of the equations for each of the fluid solid interfaces will thus cause the terms in the average over the common curve to cancel, leaving

$$\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}})}{\mathrm{D}t} - \left(\chi_s^{\overline{\overline{ws}}}J_s^{ws} + \chi_s^{\overline{\overline{ns}}}J_s^{ns}\right)\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} + \left(\varepsilon^{\overline{\overline{ws}}}\mathsf{G}^{ws} + \varepsilon^{\overline{\overline{ns}}}\mathsf{G}^{ns}\right){:}\mathbf{d}^{\overline{\overline{s}}} = 0\,. \quad (8.58)$$

According to Evolution Approximation 8.1, we also note that $J_s^{ws} = J_s^{ns}$ and $\mathsf{G}^{ws} = \mathsf{G}^{ns}$. Therefore, if we multiply Eq. (8.58) by $\chi_s^{\overline{\overline{\alpha}}}$ where $\alpha \in \mathfrak{I}_{\mathrm{cs}}^{-}$ we obtain

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - (\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}})\frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \chi_s^{\overline{\overline{\alpha}}}J_s^{\alpha}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} + \varepsilon^{\overline{\overline{\alpha}}}\mathsf{G}^{\alpha}{:}\mathbf{d}^{\overline{\overline{s}}} = 0 \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{cs}}^{-}\,, \quad (8.59)$$

where the product rule has been applied to the first term to obtain the first two time derivatives. This equation provides the evolution relation for each of the fluid-solid interfaces.

Comparison of Eq. (8.59) with Eq. (8.33) shows that

$$(\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}})\frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{\alpha}}}}{\mathrm{D}t} = \left\langle \mathbf{n}_\alpha\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{cs}}^{-}\,. \quad (8.60)$$

This last equation relates the rate of wetting of the solid to the velocity of the common curve moving across the solid surface. This equation will be used in Sect. 8.6.3 when considering common curve evolution.

8.6.2 Fluid-fluid Interface Evolution

The starting point for this derivation is Eq. (8.45). The challenge is to find suitable approximations for the last three terms on the left side of the equation in terms of macroscale properties. Answering the challenge requires that some additional approximations be stated. An appropriate set of approximations can be proposed formally as follows.

Evolution Approximation 8.2 (Fluid-fluid Interface)
The fluid-fluid interface in a two-fluid-phase porous medium system is considered to behave such that the following approximations hold:

- *the contact angle of the wn fluid-fluid interface at the solid surface is considered to be a known function of the rate and direction of wetting of the solid surface at the microscale and at the macroscale;*
- *the correlation between contact angle and other quantities can be ignored when averaging to the macroscale;*
- *the velocity of the wns common curve normal to the solid surface can be approximated as the average of the solid-phase velocity normal to the solid surface; and*

- *the rate of relaxation of the wn fluid-fluid interface to an equilibrium state is linearly dependent on the deviation of the specific wn interfacial area from its equilibrium state.*

The last item in this evolution approximation suggests a functional form for $e^{\overline{\overline{wn}}}$ in Eq. (8.45). The stipulation that the relaxation to an equilibrium state be a linear relation provides the approximation

$$e^{\overline{\overline{wn}}} = \hat{k}^{wn}\left(\varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}} - \varepsilon^{\overline{\overline{wn}}}\right) , \tag{8.61}$$

where $\hat{k}^{wn}$ is a parameter that is related to the rate of relaxation. The assumption that this relaxation to equilibrium is linear is a seemingly reasonable first approximation that can be tested using small-scale models. With this approximation invoked, Eq. (8.45) may be written

$$\begin{aligned}
&\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t} + \nabla\cdot\left[\varepsilon^{\overline{\overline{wn}}}\left(\mathbf{w}^{wn} - \mathbf{G}^{wn}\cdot\mathbf{v}^{\overline{s}}\right)\right] + \varepsilon^{\overline{\overline{wn}}}\mathbf{G}^{wn}{:}\mathbf{d}^{\overline{\overline{s}}} \\
&\quad - J_{w}^{wn}\left(\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} + \chi_{s}^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\right) - \hat{k}^{wn}\left(\varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}} - \varepsilon^{\overline{\overline{wn}}}\right) \\
&\quad - \left\langle \cos\varphi_{ws,wn}\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} \\
&\quad + \left\langle \sin\varphi_{ws,wn}\mathbf{n}_{s}\cdot\left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} = 0 .
\end{aligned} \tag{8.62}$$

It is known from pore-scale observations that the contact angle the *wn* interface makes with a solid surface depends upon the velocity of the interface in the direction tangent to the solid surface. This is typically minimally characterized as an advancing or a receding contact angle, although this quantity is more appropriately considered as a function of the tangential velocity of the interface. Evolution Approximation 8.2 states that this functional dependence of the contact angle exists at the microscale and is known. This approximation also states that the macroscale is sufficiently resolved that the correlation between the microscale angle and the microscale rate of wetting can be neglected. While this approximation is convenient, alternative approaches are possible if it is unreasonable. For example, a decomposition of the sort used for the curvature in Eq. (8.40) could be used for terms involving the contact angle, and then the term involving the deviation in the contact angle could in turn be approximated. Improved methods of treating such terms are sure to develop with continued microscale experimental and simulation research that is underway. For the purpose of this analysis, we will follow the simpler situation summarized in Evolution Approximation 8.2.

The evolution approximation allows the sine and cosine functions to be moved outside the averaging operator and be expressed in terms of macroscopic forms. As a result, Eq. (8.62) becomes

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t} + \nabla\cdot\left[\varepsilon^{\overline{\overline{wn}}}\left(\mathbf{w}^{wn} - \mathbf{G}^{wn}\cdot\mathbf{v}^{\overline{s}}\right)\right] + \varepsilon^{\overline{\overline{wn}}}\mathbf{G}^{wn}{:}\mathbf{d}^{\overline{\overline{s}}}$$

$$\begin{aligned}&-J_w^{wn}\left(\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t}+\chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\right)-\hat{k}^{wn}\left(\varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}-\varepsilon^{\overline{\overline{wn}}}\right)\\&-\cos\varphi^{\overline{\overline{\overline{ws,wn}}}}\left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}\\&+\sin\varphi^{\overline{\overline{\overline{ws,wn}}}}\left\langle\mathbf{n}_{s}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}=0\,.\end{aligned}\tag{8.63}$$

To ensure satisfaction of the identity

$$\cos^2\varphi^{\overline{\overline{\overline{ws,wn}}}}+\sin^2\varphi^{\overline{\overline{\overline{ws,wn}}}}=1\,,\tag{8.64}$$

the macroscale cosine and sine of the contact angle are defined, respectively, as

$$\cos\varphi^{\overline{\overline{\overline{ws,wn}}}}=\frac{\left\langle\cos\varphi_{ws,wn}\right\rangle_{\Omega_{wns},\Omega_{wns}}}{\left(\left\langle\cos\varphi_{ws,wn}\right\rangle^2_{\Omega_{wns},\Omega_{wns}}+\left\langle\sin\varphi_{ws,wn}\right\rangle^2_{\Omega_{wns},\Omega_{wns}}\right)^{1/2}}\tag{8.65}$$

and

$$\sin\varphi^{\overline{\overline{\overline{ws,wn}}}}=\frac{\left\langle\sin\varphi_{ws,wn}\right\rangle_{\Omega_{wns},\Omega_{wns}}}{\left(\left\langle\cos\varphi_{ws,wn}\right\rangle^2_{\Omega_{wns},\Omega_{wns}}+\left\langle\sin\varphi_{ws,wn}\right\rangle^2_{\Omega_{wns},\Omega_{wns}}\right)^{1/2}}\,.\tag{8.66}$$

The third condition given in Evolution Approximation 8.2 and the first bullet in Evolution Approximation 8.1 suggest the microscale average of the common cure velocity relative to the solid-phase velocity in the direction normal to the solid phase can be scaled to the change in the solid-phase volume fraction. The result is

$$\frac{\varepsilon^{\overline{\overline{\overline{wns}}}}}{\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}=\left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}\,.\tag{8.67}$$

From Eq. (8.60) with $\alpha = ws$ we know that

$$\left(\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t}=\left\langle\mathbf{n}_{ws}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}\,.\tag{8.68}$$

Substitution of Eqs. (8.67) and (8.68) into Eq. (8.63) gives the expression for the evolution of the *wn* interface,

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wn}}}}{\mathrm{D}t}+\nabla\cdot\left[\varepsilon^{\overline{\overline{wn}}}\left(\mathbf{w}^{wn}-\mathbf{G}^{wn}\cdot\mathbf{v}^{\overline{s}}\right)\right]+\varepsilon^{\overline{\overline{wn}}}\mathbf{G}^{wn}{:}\mathbf{d}^{\overline{s}}-J_w^{wn}\left(\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t}+\chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\right)\\&\quad-\hat{k}^{wn}\left(\varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}-\varepsilon^{\overline{\overline{wn}}}\right)-\cos\varphi^{\overline{\overline{\overline{ws,wn}}}}\left(\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t}\\&\qquad+\sin\varphi^{\overline{\overline{\overline{ws,wn}}}}\frac{\varepsilon^{\overline{\overline{\overline{wns}}}}}{\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}=0\,,\end{aligned}\tag{8.69}$$

with all averaging operators eliminated.

Terms involving the rate of change of $\varepsilon^{\overline{\overline{s}}}$ in this equation will be negligible in most cases because any solid-phase volume fraction change has a much larger time scale than the other terms in the equation. This equation reveals the dynamics of change of the fluid-fluid interfacial area. Four processes appear to be most important. First is the divergence of the normal velocity of the interface, which models the net outward volumetric flux of the interfacial area per volume. Second is the change in the fluid-phase volume fractions. When either of these fractions is zero, there will be no fluid-fluid interface; but at intermediate values, the change in volume fraction is related to the change in surface area. The third process is the relaxation of the interfacial area configuration to an equilibrium value. The fourth term is the wetting of the solid surface, a process that stretches the *wn* interface in the absence of other dynamics.

8.6.3 Common Curve Evolution

The most complete common curve kinematic equation derived to this point is Eq. (8.57). However, the last four terms in the equation require attention for the equation to become usable. We can eliminate the two averaging operators by employing Eqs. (8.67) and (8.68) so that the evolution described in Eq. (8.57) is restated as

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wns}}}}{\mathrm{D}t} + \nabla\cdot\left[\varepsilon^{\overline{\overline{wns}}}\left(\mathbf{w}^{wns} - \mathsf{G}^{wns}\cdot\mathbf{v}^{\overline{s}}\right)\right] + \varepsilon^{\overline{\overline{wns}}}\mathsf{G}^{wns}\mathbf{:}\mathbf{d}^{\overline{\overline{s}}} + \kappa_N^{wns}\frac{\varepsilon^{\overline{\overline{wns}}}}{\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}$$

$$+\,\kappa_G^{wns}\left(\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t} + e_N^{\overline{\overline{wns}}} + e_G^{\overline{\overline{wns}}} = 0\,. \tag{8.70}$$

The last two terms on the left, the relaxation terms, require additional attention.

To be able to produce a a fully macroscale description of common curve evolution by expressing the relaxation/generation terms as functions of macroscale quantities, we propose the following evolution approximation.

Evolution Approximation 8.3 (Curvature Deviation)
The common curve in a two-fluid-phase porous medium system is considered to behave such that the following approximations hold:

- *the change in the specific common curve length due to the deviation of the normal curvature of the common curve,* $e_N^{\overline{\overline{wns}}}$*, can be neglected; and*
- *the rate of relaxation of the geodesic curvature of the wns common curve is driven by the deviation of* $\varepsilon^{\overline{\overline{wns}}}$ *from its equilibrium value and is linearly related to this deviation.*

Based upon Evolution Approximation 8.3

$$e_N^{\overline{\overline{wns}}} = 0. \tag{8.71}$$

This is reasonable for most slightly compressible porous medium systems, since the compression or expansion of the solid phase will happen on a time scale that is slow compared to other dynamic processes involving the common curve.

The situation for the geodesic curvature is different. This curvature is the component of the gradient of the common curve along the common curve in the direction tangent to the solid surface. The deviation term involving the geodesic curvature in the definition of $e_G^{\overline{\overline{wns}}}$ given in Eq. (8.56) multiplies the velocity at which the common curve moves across the surface due to wetting or drying, relative to the velocity of the solid. This term will be large relative to the normal curvature deviation term that multiplies a common curve velocity relative to that of the solid phase in the direction normal to the surface. At equilibrium, $e_G^{\overline{\overline{wns}}} = 0$ because the velocities will be zero. Thus, analogously to the generation term for the *wn* interface defined in Eq. (8.61), we parameterize the generation term for the common curve as

$$e_G^{\overline{\overline{wns}}} = -\hat{k}^{wns}\left(\varepsilon_{\mathrm{eq}}^{\overline{\overline{wns}}} - \varepsilon^{\overline{\overline{wns}}}\right) , \tag{8.72}$$

where $\varepsilon_{\mathrm{eq}}^{\overline{\overline{wns}}}$ is the specific common curve length at equilibrium. Should experimental or numerical experimentation suggest a better approximation for $e^{\overline{\overline{wns}}}$, that approximation can be directly employed. With the current definition, and neglect of $e_N^{\overline{\overline{wns}}}$, Eq. (8.70) becomes

$$\begin{aligned}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{wns}}}}{\mathrm{D}t} + \nabla\cdot\left[\varepsilon^{\overline{\overline{wns}}}\left(\mathbf{w}^{wns} - \mathbf{G}^{wns}\cdot\mathbf{v}^{\overline{s}}\right)\right] + \varepsilon^{\overline{\overline{wns}}}\mathbf{G}^{wns}{:}\mathbf{d}^{\overline{\overline{s}}} + \kappa_N^{wns}\frac{\varepsilon^{\overline{\overline{wns}}}}{\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}&\\ + \kappa_G^{wns}(\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}})\frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t} - \hat{k}^{wns}\left(\varepsilon_{\mathrm{eq}}^{\overline{\overline{wns}}} - \varepsilon^{\overline{\overline{wns}}}\right) = 0\,.&\end{aligned} \tag{8.73}$$

As was the case with specific interfacial area evolution, we have formulated a closed evolution equation for the *wns* common curve in terms of macroscale variables. Also similarly to the interface evolution equations, Eq. (8.73) reveals not only the mechanisms involved with common curve evolution, but also the dependence upon other entity measures. However, a macroscale velocity of the common curve, $\mathbf{w}^{wns}$, obtained as an average of microscale components normal to the common curve appears in Eq. (8.73). Specification of this velocity requires an approximation. The velocities of the fluid-fluid interfacial area, $\mathbf{w}^{wn}$, and of the common curve, $\mathbf{w}^{wns}$, will be considered in the next section.

8.7 Average Normal Velocities

The remaining aspect of producing useful evolution equations involves developing expressions for the averages of normal velocities that appear in the interfacial area and common curve equations. To be specific, expressions are needed for $\mathbf{w}^{wn}$, which appears in Eq. (8.69), and for $\mathbf{w}^{wns}$, which appears in Eq. (8.73). These velocities are averages of the entity velocities in directions normal to the entity. Thus, these quantities differ from material velocities in the entities in two significant ways. First, even if the interface or common curve is massless, the entity itself can have a velocity. Secondly, any flow velocity within the entity tangent to the entity has no impact on the calculated value of $\mathbf{w}^{wn}$ or $\mathbf{w}^{wns}$. These macroscale entity velocities are calculated from velocities normal to any flow within the entity. Because these velocities describe geometric movement and deformation, they do not appear in conservation equations. The velocity of any material associated with *wn* and *wns* entities and the velocities of the entities themselves are distinctly different.

8.7.1 Fluid-fluid Interface Velocity Approximation

The average of the normal *wn* entity velocity needs to be defined based upon constitutive approximations, an idea that has been recognized in the literature [3]. This macroscale velocity is important during displacement processes. The microscale normal velocity of the *wn* interface and the velocity normal to that interface of any material in an adjacent fluid phase at the interface will be equal, except for cases where inter-entity mass transfer is occurring. If we consider this difference in velocities to be a second-order effect with regard to other terms in the evolution equations, we can posit the macroscale normal interfacial velocity as being dependent upon the orientation of the interface and the velocity of the fluids. Thus, we propose the following evolution approximation.

Evolution Approximation 8.4 (Interface Velocity)
The normal velocity of the wn interface can be approximated constitutively as a linear combination of the average density-weighted normal velocities of the bounding fluids that form the interface in the averaged macroscale normal direction with the orientation tensor impacting the direction.

Based on the definition of $\mathbf{w}^{wn}$ given in Eq. (8.38), we know that

$$\mathbf{w}^{wn} - \mathsf{G}^{wn}\cdot\mathbf{v}^{\overline{s}} = \left\langle \mathsf{G}_{wn}\cdot\left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega_{wn}} . \tag{8.74}$$

The average velocity of an adjacent fluid phase over the *wn* interface is not generally equal to the average velocity over the phase. However, the fact that only the normal component of the material velocity at the interface is of importance suggests that the macroscale interface velocity may be expressed constitutively, in accord with Evolution Approximation 8.4, as

$$\mathbf{w}^{wn} - \mathsf{G}^{wn}\cdot\mathbf{v}^{\overline{s}} = \mathsf{G}^{wn}\cdot\left[\hat{A}^{w}\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) + \hat{A}^{n}\left(\mathbf{v}^{\overline{n}} - \mathbf{v}^{\overline{s}}\right)\right] . \tag{8.75}$$

The interfacial velocity coefficients $\hat{A}^{w}$ and $\hat{A}^{n}$ are likely functions of the ratio of dynamic viscosities of the fluids $\hat{\mu}_{w}/\hat{\mu}_{n}$ and the wetting fluid phase saturation $s^{\overline{\overline{w}}}$.

Consideration of Eqs. (8.74)–(8.75) suggests that the $\hat{A}^w + \hat{A}^n$ is of order 1. The dependence of these coefficients on the system parameters is fertile ground for future research.

8.7.2 Common Curve Velocity Approximation

Similar reasoning to that for the *wn* interface can be used to deduce a constitutive form for the macroscale velocity of the common curve. The microscale normal velocity of a common curve has two non-zero components. One of these components is in the direction normal to the solid surface, and the other is tangent to the solid surface. As discussed in consideration of the normal and geodesic curvatures, it is reasonable to expect that the component tangent to the solid surface is dominant and that the velocity of the curve will be related to the velocity of the fluids while considering this orientation. Thus we propose an evolution approximation as follows.

Evolution Approximation 8.5 (Common Curve Velocity)
The normal velocity of the wns common curve is dominated by the component tangent to the solid surface, which can be approximated as a linear combination of the macroscale velocities of the w and n fluids and the macroscale orientation tensor of the dominant direction.

Based upon the definition of $\mathbf{w}_{wns}$ given in Eq. (8.51) with an intrinsic average, $\mathbf{w}^{wns}$, the expression for the macroscale velocity relative to the solid is

$$\mathbf{w}^{wns} - \mathsf{G}^{wns} \cdot \mathbf{v}^{\overline{s}} = \left\langle \mathsf{G}_{wns} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns}, \Omega_{wns}} . \tag{8.76}$$

When the macroscale orientation tensor obtained from $\mathbf{n}_s \mathbf{n}_s$ is the same regardless of whether it is integrated over the entire solid surface, the *ws* portion of the solid surface, the *ns* portion of the solid surface, or the *wns* common curve, evaluation of the averaging operation suggests, in light of Evolution Approximation 8.5, that

$$\mathbf{w}^{wns} - \mathsf{G}^{wns} \cdot \mathbf{v}^{\overline{s}} = \left(\mathsf{G}^{wns} - \mathsf{G}^{ws} \right) \cdot \left[\hat{B}^w \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}} \right) + \hat{B}^n \left(\mathbf{v}^{\overline{n}} - \mathbf{v}^{\overline{s}} \right) \right] , \tag{8.77}$$

where $\hat{B}^w$ and $\hat{B}^n$ are common curve velocity parameters that are expected to depend upon some combination of fluid viscosities and saturation. The factor $\mathsf{G}^{wns} - \mathsf{G}^{ws}$ is intended to account for the fact that the movement of the common curve tangentially to the surface is dominant. Common curve movement is a higher order effect than movement of the *wn* interface velocity. This implies that crudeness in the approximations that went into Eq. (8.77) will negatively impact the system model less than shortcomings in approximations that went into Eq. (8.75).

8.8 Summary

In this chapter, we have formulated a set of evolution equations for geometric densities that can be used as a component of a closed TCAT model. These equations are approximate, and they are not based upon conservation principles, because quantities such as the extent of specific interfacial areas and specific common curve lengths are not conserved physical quantities. Rather, mechanisms exist that lead to the formation and destruction of these entity domains as they translate and deform. To derive these macroscale evolution equations, we relied upon the averaging theorems, which are exact expressions. These averaging theorems assisted in establishing a framework for the evolution equations and in revealing the mathematical forms of the operative mechanisms that must be accounted for. This formulation also revealed the coupled nature of the entity measures. To assist in producing closed, solvable evolution equations, sets of approximations have been formally presented. An additional component of this analysis is the approximation of the macroscale velocities of a fluid-fluid interface and of the common curve in a two-fluid-phase system. These approximations account for the fact that the velocity of these domains is different from the velocity of material within the domains such that only movement normal to the domain contributes to its macroscopic representation.

For single-fluid-phase porous medium flow, the relation between the change in the surface area density of the solid phase and the solid-phase volume fraction was obtained as Eq. (8.20). Because the solid-phase movement and deformation is considered to be independent of the fluids that contact it, this equation is also applicable to two-fluid-phase flow, making use of the notational modification employed in Eq. (8.58). For this case, the evolution equations for the $\varepsilon^{\overline{\overline{ws}}}$ and $\varepsilon^{\overline{\overline{ns}}}$ portions of the solid surface area are provided in Eq. (8.59). In that equation these surface area densities are related to the change in volume fraction of the solid phase and the wetting of the solid surface.

For the more complex two-fluid case, an interface between the fluids as well as a common curve on the solid surface must be accounted for. Approximations employed in conjunction with averaging theorems led to Eq. (8.69) for the rate of change of $\varepsilon^{\overline{\overline{wn}}}$. This change is related, primarily, to changes in the distribution of the fluid volume fractions, the relaxation of the interface to an equilibrium configuration, and the rate of wetting of the solid surface. The common curve evolution equation is given in Eq. (8.73). This equation is based on the averaging theorems applied to a common curve and relates the change in common curve length density to the rate of solid wetting and the relaxation of the common curve shape. In both of these equations, coefficients appear that macroscopically account for the orientations of the entities, rates of relaxation of the entities to an equilibrium configuration, and the curvatures of the entity domains. Accounting for these parameters can be challenging, but their importance in accurately characterizing entity deformation is indisputable.

Perhaps the most difficult quantities to model are the macroscale velocities that account for displacement of the *wn* interface and the *wns* common curve. The fact that these velocities are not simply equal to the velocities of material within them has been emphasized because errors have been made as a result of overlooking this detail [10–12]. Without additional experimental or computational study, the most reasonable approximation is to expect that these velocities are related to the fluid velocities, with the suggested representation for the *wn* velocity given in Eq. (8.75) and that for the *wns* velocity appearing in Eq. (8.77). The directions of flow are important elements of these approximations. For example, fluid flow tangent to a *wn* interface will not contribute to the velocity of that interface. However, fluid flow normal to the interface will cause it to translate and deform.

Because approximations are needed to develop and close the evolution equations, it is important to be willing to revisit these approximations. Modern and evolving experimental and computational methods provide a means to study model systems at the microscale. In many cases, the validity of the approximations made can be evaluated in detail using these microscale analysis tools. Such analysis is important for verification of the approximations enumerated and for improving these approximations where necessary. We note that this feature is different from the derivation of the general conservation and balance equations and the thermodynamic relations. These are derived without approximations, although they do require approximate closure relations for use in modeling.

At this point, we have in place all of the components needed to formulate closed, macroscale TCAT models. The chapters that follow will make use of these components to deduce relatively simple TCAT models for single-fluid-phase flow in porous media, species transport in single-fluid-phase porous media, and two-fluid-phase flow in porous media.

Exercises

8.1. Consider a porous medium composed of spherical solid particles that are incompressible and do not deform. The medium itself, however, does deform because of a readjustment of the sphere packing. Make use of the evolution relation given as Eq. (8.20) to show that $\varepsilon^{\overline{\overline{ws}}}/\varepsilon^{\overline{\overline{s}}}$ is a constant.

8.2. Simplify Eq. (8.69) for the case of steady flow in a rigid solid. Discuss the physical meaning of the surviving terms.

8.3. Simplify Eq. (8.73) for the case where the solid-phase dynamics are much slower than the common curve dynamics.

8.4. Consider Eq. (8.75) for the fluid-fluid interface velocity for the case where the solid phase may be consider to be rigid. Describe the physical setting in which $\mathbf{w}_{wn} = 0$ but neither $\mathbf{v}^{\overline{w}}$ nor $\mathbf{v}^{\overline{n}}$ is zero.

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Chapter 9
Single-fluid-phase Flow

9.1 Overview

The goal of this chapter is to formulate a set of closed, solvable, macroscale, single-fluid-phase flow models using the TCAT approach. This is the first macroscale TCAT application to be considered. Fig. 9.1 indicates the elements of the TCAT framework that form the basis of this chapter. These same elements will be employed in subsequent chapters for analysis of chemical species transport and two-fluid-phase flow, although details of the equations and assumptions invoked will be different for each application instance.

With regard to Fig. 9.1, it can be seen that elements on the left side of the full figure have been dimmed. These elements are concerned with transformation from the microscale to the larger scale of the entropy inequality, conservation equations, equilibrium conditions, and thermodynamic relations. The formulation of these microscale relations and the utilization of averaging theorems to accomplish the transformation to the macroscale have been the subjects of previous chapters. Additionally, the development of geometric relations was the topic of the last chapter. Thus, here, and in subsequent chapters, we can consider all basic macroscale relations to be available. The task to be addressed is the combination of these equations to obtain closure relations and a hierarchy of closed models.

The larger-scale components can be assembled to derive a wide range of TCAT models. These models can describe systems with various numbers of fluid and solid phases, interfaces between phases, common curves where interfaces meet, and common points where common curves meet. The models can be proposed with different levels of detail with regard to accounting for chemical species present, properties of interfaces, common curves, common points, and complexity of the closure relations. Models that do not explicitly account for compositional changes in the fluids and solids due to diffusion and dispersive processes are commonly referred to as flow models. Transport models account for compositional changes as well as for bulk phase movement. In the present chapter, we will develop a flow model and not

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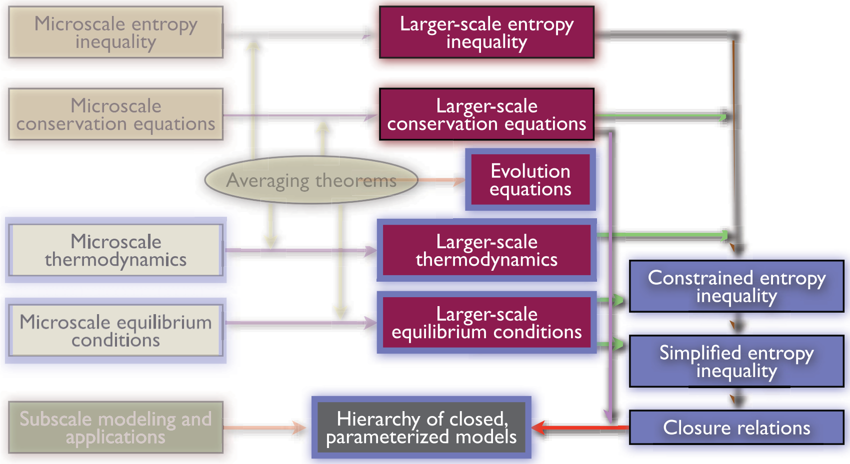

Fig. 9.1 TCAT elements of interest in Chap. 9 for closing macroscale single-fluid-phase flow equations (after [4])

be concerned with variations in composition due to differences in the velocities of various chemical species or to chemical reactions.

The major steps associated with employing the macroscale equations in the TCAT approach to construct a specific model are indicated by the arrows in the right half of Fig. 9.1. The first step involves constraining the entropy inequality with conservation and thermodynamic conditions. The second step simplifies the constrained entropy inequality by applying some assumptions that are consistent with system behavior so that the entropy generation term is obtained as a set of products of independent forces and fluxes that are zero at equilibrium. Then the form of the simplified entropy inequality is employed to infer the forms of closure relations that can be substituted into the conservation equations to obtain closed models. These steps are essentially the same as those employed in Chap. 5 to obtain closed microscale models, as depicted in Fig. 5.1. The primary difference is that the present chapter makes use of macroscale relations, while the former chapter sought microscale closed equations.

The TCAT approach employs an explicit formal structure to identify the restrictions placed on the system, the approximations applied, and the elements of the model developed. This structure is important because it provides a path for reexamining assumptions that may be responsible for a model being unable to describe a system of interest. The kinds of assumptions employed have been classified so that the TCAT approach is well organized, and leading opportunities for improvement of models can be found relatively easily. These assumption types are denoted as primary restrictions, secondary restrictions, simplified entropy inequality (SEI) approximations, and closure approximations.

Primary restrictions stipulate the thermodynamic theory relied upon and the properties of the porous medium model (e.g., the dimensionality of the model). Additionally, after formulation of a general entropy inequality (EI) augmented by a set of conservation equations using Lagrange multipliers, primary restrictions are imposed on selection of values for the Lagrange multipliers. These restrictions identify the entities to be modeled explicitly, indicate the degree and rigor with which chemical species properties, as opposed to the properties on an entity as a whole, are to be modeled, and facilitate the arrangement of the EI into force-flux form to the extent possible without introducing approximations. The resulting equation is called the constrained entropy inequality (CEI). Simplified entropy inequality (SEI) approximations are needed to arrive at a strict force-flux form of the EI. While these approximations are necessary and are selected with the intention that they be physically appropriate, they do introduce some error into the formulation. If this error is found to be non-negligible, the SEI approximations may be revisited and reformulated based on evidence gleaned from experimental or numerical studies as well as rethinking of the rationale behind the approximations. Subsequently, secondary restrictions are imposed, if desired, to further constrain the CEI by eliminating some of the processes that are not of interest for a particular application. This simplifies the task of closing the model. For example, a system might be limited to being isothermal by a secondary restriction, thereby making determination of a closure relation for the non-advective heat flux vector unnecessary. Identification of possible closure approximations from a broad set of permissible relations is informed by the SEI. The selection of alternative sets of closure relations yields a hierarchy of closed models of varying sophistication.

The sections that follow in this chapter illustrate the application of TCAT model formulation using the template described above for single-fluid-phase flow in a porous medium. While the model to be formulated is relatively simple, it provides both a useful result as well as a convenient means to demonstrate the TCAT model formulation process with minimal complexity.

9.2 Single-phase-flow System Definition

In principle, one can apply TCAT to develop a model for a complicated many-fluid-phase-flow case with species transport and reactions under non-isothermal conditions. Limiting cases of such a model would reduce to common applications of concern—all the way down to isothermal single-fluid-phase flow. This approach is elegant but requires the complexity associated with deriving a CEI for a multifaceted system. Alternatively, very specific TCAT models can be specified and formulated for each application. This approach is the simplest possible way to develop a TCAT model for a given application, but it requires a completely new TCAT formulation for every single extension of complexity of the application. A middle ground between the most general and most specific approaches is to define a system for which a class of model is developed that is sufficiently broad to encompass the description of many applications, but sufficiently narrow to allow a formulation without excessive complexity; we follow this middle ground.

To identify the elements of the system that will be modeled, we make use of primary restrictions. These establish the entities that will be modeled, the length scale of the model, the phenomena to be modeled, and the proposed thermodynamic formalism that will be employed. Selection of these model elements is a fundamental decision that is made at the beginning of the model development and serves to bound the class of TCAT models formulated. For the present chapter, the system is identified by invoking three primary restrictions.

The first primary restriction identifies the entities to be modeled and the scale of modeling.

Primary Restriction 9.1 (System and Scale)
The system of concern consists of a single fluid phase w, a relatively immobile solid phase s, and an interface ws between the two phases. The spatial scale of concern is the macroscale, ℓ^{ma}*, with* $\ell^{\mathrm{r}}_{\mathrm{r}} \ll \ell^{\mathrm{ma}} \ll \ell^{\mathrm{me}}$*, where* $\ell^{\mathrm{r}}_{\mathrm{r}}$ *and* ℓ^{me} *are the resolution scale and megascale of the system, respectively.*[1] *The domain of the system is* Ω *with boundary* Γ*.*

The stipulation in Primary Restriction 9.1 that the solid phase is relatively immobile indicates that we are studying a porous medium system rather than a problem such as sediment transport where the solid phase velocity is of the same order of magnitude as the fluid velocity. The single fluid phase in the specified system completely fills the pore space. Because the model is restricted to be at the macroscale, the microscale juxtaposition of phases is not explicitly accounted for. Rather, the phases and interfaces exist at all points in the domain Ω, and their extent will be accounted for by volume and area densities. Finally, Primary Restriction 9.1 specifies that the models are developed for the case where the system length scales are well separated. Thus the macroscale conservation and thermodynamic equations are those obtained by averaging over an REV of length scale ℓ^{ma} throughout the domain. A fully macroscale model involves three spatial dimensions and time. For this macroscale formulation, with wide separation of scales, all model parameters have well-defined averages that are local in nature and not dependent upon the scale or the boundary conditions of the system being considered. In other words, the models to be developed will be deterministic and will meet the standard continuum requirements previously discussed.

We observe that many natural systems exist that contain heterogeneities such that they do not satisfy the conditions of Primary Restriction 9.1. In particular, the deterministic framework may be overly restrictive and of limited applicability. On the other hand, the intention here is to derive models for well-defined systems, and systems that satisfy Primary Restriction 9.1 certainly exist. By working with well-defined, deterministic systems here, TCAT models will be formulated that represent physical phenomena that are operative in those systems with sufficient fidelity. Because these fundamental models can be extended, for instance by beginning with a

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[1] The descriptions of length scales are provided in the discussion of Eq. (1.1).

relaxed primary restriction set, the fundamental TCAT model formulation approach is demonstrated and accomplished without a loss of generality.

The second primary restriction is concerned with the transport processes to be modeled.

Primary Restriction 9.2 (Phenomena Modeled)
The phenomena of concern consist of the transport of mass, momentum, and energy in each of the entities. Transport phenomena of various chemical species within an entity will not be modeled explicitly.

Primary Restriction 9.2 specifies that conserved quantities will be modeled for each entity as a whole without consideration of compositional effects. Thus transport equations for individual chemical species will not be formulated. Rather the conservation equations will apply to each entity as a whole while also allowing for exchanges of properties between entities. The resulting single-phase-flow model will apply to isothermal as well as non-isothermal systems, and the distinctly different behavior of the fluid and solid phases will be accounted for. Although Primary Restriction 9.1 has limited the system to being a porous medium, no constraint has been imposed on the fluid flow regime. Both creeping flow and flow at higher Reynolds numbers may be considered because no terms are eliminated from the conservation equations by Primary Restriction 9.2. Explicit inclusion of conservation equations for the interface between phases ensures that the properties of that interface that impact system behavior will be accounted for as an aid to fundamental understanding.

The third primary restriction to be employed relates to the thermodynamic description of the system. This is important as it impacts the material properties of the system.

Primary Restriction 9.3 (Thermodynamic Theory)
Classical irreversible thermodynamics (CIT) is employed to describe the thermodynamic behavior of the system entities at equilibrium and near-equilibrium states. The solid phase is modeled as elastic.

TCAT makes use of a thermodynamic theory to connect variables appearing in the EI with those appearing in the conservation equations. The specification of the CIT formalism means that the microscale approach described in Chap. 3 along with the equilibrium conditions of Chap. 4 will be employed in their macroscale versions as derived in Chap. 7. Although other thermodynamic theories exist, as alluded to in Sect. 3.12, experience has shown that CIT is an adequate foundation for many systems investigated to date. We can support the choice of CIT with decades of successful comparisons between theory and experiment and more recently with validity that can be established through comparison to statistical mechanical approaches and molecular scale computations. By averaging CIT to the macroscale, we have ensured connection across scales and well-defined variables at the macroscale. Stipulating that the solid behaves elastically at the microscale imposes a constraint on the thermodynamic behavior of individual grains in the porous medium but does not constrain the macroscale behavior of the porous medium solid to being elastic.

Settling may take place due to rearrangement of the grains without the properties of any of the grains changing.

9.3 Conservation and Thermodynamic Equations

TCAT models are built upon systems of conservation and balance equations for each entity in the system. The primary restrictions establish the physical processes that must be accounted for in formulating a particular class of model. The conservation equations, balance equations for body force potential and entropy, and the thermodynamic relations have been derived in previous chapters. Here, we will select and combine the equations appropriate for the system described by the primary restrictions of the last section. Because the TCAT method is a systematic procedure, it should not be surprising that the development of macroscale models will follow the same steps employed in Chap. 5 when developing a microscale model. Thus, the structure of the current section will be similar to that of Sect. 5.3. The formulation will be developed in accord with the boxes highlighted in Fig. 9.1. We will first identify the general set of equations needed, and then simplify the set based on the primary restrictions noted above. The equations have been derived in previous chapters and thus will be only referred to here in general terms until some mathematical manipulation is needed.

9.3.1 Entropy Inequality

The large scale EI is the element of the formulation at the top of Fig. 9.1. In general, a system is composed of multiple species that may appear in the full set of entities. We select the material derivative form of the entropy inequality as provided in Table 6.2 or Eq. (6.134). Thus the complete set of entropy inequalities may be expressed as

$$\mathcal{S}_{*}^{\overline{\overline{i\alpha}}} = \Lambda^{\overline{\overline{i\alpha}}} \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I} \, . \tag{9.1}$$

In this equation, $\Lambda^{\overline{\overline{i\alpha}}}$ is the rate of entropy production per volume at a point associated with species i in entity α due to irreversible processes. Although the entropy production for processes associated with a particular species may be negative, and the sign of the entropy production in an entity associated with inter-entity entropy transfer is not known, the net production of entropy due to all irreversible processes at a point will be non-negative. Thus if we sum over all entities and species we obtain

$$\sum_{\alpha \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \mathcal{S}_{*}^{\overline{\overline{i\alpha}}} = \sum_{\alpha \in \mathcal{I}} \sum_{i \in \mathcal{I}_s} \Lambda^{\overline{\overline{i\alpha}}} \geq 0 \, . \tag{9.2}$$

However, we know that the sum of the species-based entropy balance over all species is equal to the entity-based balance such that

$$\mathcal{S}_*^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathcal{S}_*^{\overline{\overline{i\alpha}}} \tag{9.3}$$

and

$$\Lambda^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \Lambda^{\overline{\overline{i\alpha}}} . \tag{9.4}$$

The expanded expression for the elements that contribute to the entropy production of an entity, $\mathcal{S}_*^{\overline{\overline{\alpha}}}$, may be written directly from the next to the last row of Table 6.3.

In the current chapter, we are interested in modeling the behavior of entities and will not be concerned with species-based equations. In these instances, the EI may be written by substituting Eqs. (9.3) and (9.4) into Eq. (9.2) to obtain

$$\sum_{\alpha \in \mathfrak{I}} \mathcal{S}_*^{\overline{\overline{\alpha}}} = \sum_{\alpha \in \mathfrak{I}} \Lambda^{\overline{\overline{\alpha}}} > 0 . \tag{9.5}$$

The next task is to provide appropriate constraints for this basic inequality.

9.3.2 Conservation Equations

Fig. 9.1 indicates that the larger-scale conservation equations comprise one set of constraints to be applied to Eq. (9.5). Macroscale conservation equations for mass, momentum, and energy of each chemical species have been provided in Table 6.2. These equations, expressed in material derivative form, are employed in this analysis and are written for species mass, species momentum, and species energy, respectively, as

$$\mathcal{M}_*^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I} , \tag{9.6}$$

$$\boldsymbol{\mathcal{P}}_*^{\overline{\overline{i\alpha}}} = \mathbf{0} \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I} , \tag{9.7}$$

and

$$\mathcal{E}_*^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I} . \tag{9.8}$$

An additional equation in Table 6.2 will be employed that provides the impact of the gravitational potential on a chemical species. This equation has the form

$$\mathcal{G}_*^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I} . \tag{9.9}$$

As has been mentioned previously, this is not strictly a conservation equation but is a balance expression obtained as a hybrid of the mass conservation equation and the relation between the gravitational potential and gravity.

In the present chapter, we are ignoring the transport of chemical species within the entity. Thus, rather than using species based equations, we will simplify the conservation and balance equations by summing over all species. Summation of

Eqs. (9.6)–(9.9) over the chemical species provides the corresponding set of entity-based equations

$$\mathcal{M}_*^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathcal{M}_*^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{I} \,, \tag{9.10}$$

$$\mathcal{P}_*^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathcal{P}_*^{\overline{\overline{i\alpha}}} = \mathbf{0} \quad \text{for } \alpha \in \mathfrak{I} \,, \tag{9.11}$$

$$\mathcal{E}_*^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathcal{E}_*^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{I} \,, \tag{9.12}$$

and

$$\mathcal{G}_*^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathcal{G}_*^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{I} \,. \tag{9.13}$$

The entity-based equations may be found in Table 6.3 and are the forms that will be used for the analysis of single-phase-fluid flow. As has been confirmed in Chap. 6, these entity-based equations may be obtained by summation over their species-based counterparts, as indicated in Eqs. (9.10)–(9.13) or obtained directly by applying the averaging theorems to the microscale equations for each entity.

9.3.3 Thermodynamic Relations

Based on Fig. 9.1, the larger-scale thermodynamics also provide some constraints on the EI. As was stated in Primary Restriction 9.3, we will employ the macroscale CIT framework. The macroscale relations have been obtained in Chap. 7. Different thermodynamic expressions for the rate of change of energy are needed for a fluid, a solid, and the interface between them. The equations are rather long. Thus, rather than being collected in a table, these equations are referenced according to where they have been derived in the text in Table 7.2. For a species in any entity, the dynamic thermodynamic relation is expressed as

$$\mathcal{T}_*^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I} \,. \tag{9.14}$$

The particular form for a fluid phase is given in Eq. (7.44); for the solid phase, the thermodynamic expression is Eq. (7.78); and for the interface, $\mathcal{T}_*^{\overline{\overline{i\alpha}}}$ is given by Eq. (7.92).

Because the species-based formulation is not employed for the conservation equations, it need not be employed for the thermodynamic relations either. Thus, these relations are summed over all species to obtain

$$\mathcal{T}_*^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathcal{T}_*^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{I} \,. \tag{9.15}$$

The constraints on the EI are provided by $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ for each entity and are stated as Eqs. (7.54), (7.80), and (7.96) for the fluid phase, solid, and interface, respectively.

In the same way that internal energy appears in both a conservation equation and a thermodynamic relation, the body force potential is used in two places. The body force potential equations that have character similar to a thermodynamic expression are tabulated by equation number in Table 7.2. These equations are written as

$$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } i \in \mathfrak{I}_s, \alpha \in \mathfrak{I} \,. \tag{9.16}$$

with particular forms for the fluid, solid, and interface entities given by Eqs. (7.47), (7.79), and (7.95), respectively.

These equations are also summed over all species for the present application according to

$$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}} = \sum_{i \in \mathfrak{I}_s} \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{I} \,. \tag{9.17}$$

The entity-based equations indicated are identified in Table 7.2 as Eqs. (7.58), (7.81), and (7.97), respectively, for the fluid, solid, and interface entity.

9.4 Constrained Entropy Inequality

According to Fig. 9.1, the equations identified in the last section should be combined to form the CEI. The conservation and thermodynamic relations supplement the basic EI by providing additional physical conditions that must be satisfied during an entropy generation process. We note that each of these conditions is written as some group of terms that sums to zero. Thus they can be multiplied by an arbitrary coefficient and added on to the basic EI without changing the entropy generation rate prediction. Selection of the coefficients in a judicious way can lead to an expression for the entropy generation as a product of forces and fluxes.

9.4.1 Augmented Entropy Inequality

The general augmented macroscale EI consists of the basic EI of Eq. (9.2) constrained by the full set of species-based conservation and thermodynamic equations. This inequality is expressed as

$$\sum_{\alpha \in \mathfrak{I}} \sum_{i \in \mathfrak{I}_s} \mathcal{S}_*^{\overline{\overline{i\alpha}}} + \sum_{\alpha \in \mathfrak{I}} \sum_{i \in \mathfrak{I}_s} \lambda_{\mathcal{E}}^{i\alpha} \mathcal{E}_*^{\overline{\overline{i\alpha}}} + \sum_{\alpha \in \mathfrak{I}} \sum_{i \in \mathfrak{I}_s} \boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{i\alpha} \cdot \boldsymbol{\mathcal{P}}_*^{\overline{\overline{i\alpha}}} + \sum_{\alpha \in \mathfrak{I}} \sum_{i \in \mathfrak{I}_s} \lambda_{\mathcal{M}}^{i\alpha} \mathcal{M}_*^{\overline{\overline{i\alpha}}}$$
$$+ \sum_{\alpha \in \mathfrak{I}} \sum_{i \in \mathfrak{I}_s} \lambda_{\mathcal{G}}^{i\alpha} \mathcal{G}_*^{\overline{\overline{i\alpha}}} + \sum_{\alpha \in \mathfrak{I}} \sum_{i \in \mathfrak{I}_s} \lambda_{\mathcal{T}}^{i\alpha} \mathcal{T}_*^{\overline{\overline{i\alpha}}}$$

$$+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda^{i\alpha}_{\mathcal{T}\mathcal{G}}\mathcal{T}^{\overline{\overline{i\alpha}}}_{\mathcal{G}*}=\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\Lambda^{\overline{\overline{i\alpha}}}\geq 0\,, \tag{9.18}$$

where the subscripted and superscripted λ and $\boldsymbol{\lambda}$ coefficients are the Lagrange multipliers. The stipulation of Primary Restriction 9.2 that the species behavior within an entity will not be explicitly modeled can be honored by requiring that a Lagrange multiplier for a particular equation describing a process in an entity be the same for all chemical species within that entity. Thus, the qualifier *i* can be removed from all the Lagrange multipliers, which can then be moved outside the summations over all species, such that Eq. (9.18) becomes

$$\begin{aligned}\sum_{\alpha\in\mathfrak{I}}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{S}^{\overline{\overline{i\alpha}}}_{*}\right)+\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{E}}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{E}^{\overline{\overline{i\alpha}}}_{*}\right)+\sum_{\alpha\in\mathfrak{I}}\boldsymbol{\lambda}^{\alpha}_{\boldsymbol{\mathcal{P}}}\cdot\left(\sum_{i\in\mathfrak{I}_s}\boldsymbol{\mathcal{P}}^{\overline{\overline{i\alpha}}}_{*}\right)&\\ +\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{M}}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{M}^{\overline{\overline{i\alpha}}}_{*}\right)+\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{G}}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{G}^{\overline{\overline{i\alpha}}}_{*}\right)+\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{T}}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{T}^{\overline{\overline{i\alpha}}}_{*}\right)&\\ +\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{T}\mathcal{G}}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{T}^{\overline{\overline{i\alpha}}}_{\mathcal{G}*}\right)=\sum_{\alpha\in\mathfrak{I}}\left(\sum_{i\in\mathfrak{I}_s}\Lambda^{\overline{\overline{i\alpha}}}\right)\geq 0\,.&\end{aligned} \tag{9.19}$$

Each of the summations over the species that is in parentheses in this equation has been discussed in Sect. 9.3 and produces an entity-based equation. Thus we can replace these summations with the entity-based equations to obtain

$$\begin{aligned}\sum_{\alpha\in\mathfrak{I}}\mathcal{S}^{\overline{\overline{\alpha}}}_{*}+\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{E}}\mathcal{E}^{\overline{\overline{\alpha}}}_{*}+\sum_{\alpha\in\mathfrak{I}}\boldsymbol{\lambda}^{\alpha}_{\boldsymbol{\mathcal{P}}}\cdot\boldsymbol{\mathcal{P}}^{\overline{\overline{\alpha}}}_{*}+\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{M}}\mathcal{M}^{\overline{\overline{\alpha}}}_{*}&\\ +\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{G}}\mathcal{G}^{\overline{\overline{\alpha}}}_{*}+\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{T}}\mathcal{T}^{\overline{\overline{\alpha}}}_{*}+\sum_{\alpha\in\mathfrak{I}}\lambda^{\alpha}_{\mathcal{T}\mathcal{G}}\mathcal{T}^{\overline{\overline{\alpha}}}_{\mathcal{G}*}=\sum_{\alpha\in\mathfrak{I}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,.&\end{aligned} \tag{9.20}$$

For the single-fluid-phase case under consideration, $\mathfrak{I}=\{w,s,ws\}$. With the equations corresponding to the notation indicated, Eq. (9.20) is the augmented EI for single-phase flow.

9.4.2 Selection of Lagrange Multipliers

To complete the formulation of the CEI, values for the Lagrange multipliers in Eq. (9.20) must be determined. Because $\boldsymbol{\lambda}^{\alpha}_{\boldsymbol{\mathcal{P}}}$ is a vector, we see that there are eight scalar values for the multipliers associated with each entity so that 24 Lagrange coefficients can be specified. Regardless of the values selected, the equality will be correct since the sum of the terms in each of the supplemental equations is equal to 0. The selection of the coefficients does impact how the the entropy generation is modeled but does not impact its value.

Because we seek to represent the entropy generation as a sum of force-flux pairs, we will select the Lagrange multipliers such that the material derivatives are eliminated. Equations for $\mathcal{S}_*^{\overline{\overline{\alpha}}}$, $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, $\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$, $\mathcal{M}_*^{\overline{\overline{\alpha}}}$, and $\mathcal{G}_*^{\overline{\overline{\alpha}}}$ are taken from Table 6.3. Equation numbers for $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$ are pointed to in Table 7.2 for the needed thermodynamic relations for fluid, solid, and interface entities. Each entity is modeled as composed of a single chemical species.

Substitution of the expanded equations into Eq. (9.20) produces a very long equation. Because we are interested in selecting the Lagrange multipliers such that the material time derivatives are eliminated to the degree possible, only the material derivatives are indicated in the next equation with the remaining terms, which will be dealt with subsequently, designated using ellipses. Thus Eq. (9.20) is expanded to

$$\begin{aligned}
&\sum_{\alpha\in\mathfrak{I}}\left[\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\ldots\right]+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{E}}^{\alpha}\left\{\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left[E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)\right]+\ldots\right\}\\
&+\sum_{\alpha\in\mathfrak{I}}\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{\alpha}\cdot\left[\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}})}{\mathrm{D}t}+\ldots\right]+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{M}}^{\alpha}\left[\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t}+\ldots\right]\\
&+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{G}}^{\alpha}\left[\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\ldots\right]+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{T}}^{\alpha}\left[\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\mu^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t}+\ldots\right]\\
&+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{T}\mathcal{G}}^{\alpha}\left[\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\psi^{\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t}+\ldots\right]=\sum_{\alpha\in\mathfrak{I}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. \qquad (9.21)
\end{aligned}$$

The product rule may be employed to expand out the material derivatives in this equation, for example by writing

$$\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\right)=\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\cdot\frac{\mathrm{D}^{\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}}{\mathrm{D}t}\,, \qquad (9.22)$$

so that the full set of unique material derivatives may be seen to be

$$\mathfrak{D}=\left\{\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}K_E^{\overline{\overline{\alpha}}}}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}\right\}\quad\text{for }\alpha\in\mathfrak{I}\,. \qquad (9.23)$$

In this set, the fourth term is a derivative of a vector and thus consists of three elements. Therefore, there are eight material derivatives for each of the three entities in the system for a total of 24 material derivatives. For these derivatives to be eliminated from Eq. (9.21), the groupings of the 24 Lagrange multipliers that form the coefficients of each of these derivatives must be zero.

Rearrangement of Eq. (9.21) by collecting the multipliers of the derivatives provides

$$\sum_{\alpha\in\mathfrak{I}}\left(1-\theta^{\overline{\overline{\alpha}}}\lambda_{\mathcal{T}}^{\alpha}\right)\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\sum_{\alpha\in\mathfrak{I}}\left(\lambda_{\mathcal{E}}^{\alpha}+\lambda_{\mathcal{T}}^{\alpha}\right)\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}$$

$$
\begin{aligned}
&+\sum_{\alpha\in\mathfrak{J}}\left[\lambda_{\mathcal{E}}^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)+\boldsymbol{\lambda}_{\mathcal{P}}^{\alpha}\cdot\mathbf{v}^{\overline{\alpha}}+\lambda_{\mathcal{M}}^{\alpha}-\lambda_{\mathcal{T}}^{\alpha}\mu^{\overline{\alpha}}-\lambda_{\mathcal{TG}}^{\alpha}\psi^{\overline{\alpha}}\right]\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t}\\
&+\sum_{\alpha\in\mathfrak{J}}\left(\lambda_{\mathcal{E}}^{\alpha}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}+\boldsymbol{\lambda}_{\mathcal{P}}^{\alpha}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\right)\cdot\frac{\mathrm{D}^{\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}}{\mathrm{D}t}+\sum_{\alpha\in\mathfrak{J}}\lambda_{\mathcal{E}}^{\alpha}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\frac{\mathrm{D}^{\overline{\alpha}}K_E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}\\
&+\sum_{\alpha\in\mathfrak{J}}\left(\lambda_{\mathcal{G}}^{\alpha}+\lambda_{\mathcal{TG}}^{\alpha}\right)\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\sum_{\alpha\in\mathfrak{J}}\cdots=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. \qquad (9.24)
\end{aligned}
$$

Here it is seen that the material derivative of $K_E^{\overline{\overline{\alpha}}}$ cannot be eliminated except by setting $\lambda_{\mathcal{E}}^{\alpha}=0$, which would eliminate the energy equation as a constraint on the system and also make it impossible to eliminate the material derivative of the entropy. Therefore, we will allow this term to survive and deal with it elsewhere in the formulation. By inspection, the multipliers of the remaining time derivatives will be zero if, for $\alpha\in\mathfrak{J}$,

$$\lambda_{\mathcal{T}}^{\alpha}=\frac{1}{\theta^{\overline{\overline{\alpha}}}}\,, \qquad (9.25)$$

$$\lambda_{\mathcal{E}}^{\alpha}=-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\,, \qquad (9.26)$$

$$\boldsymbol{\lambda}_{\mathcal{P}}^{\alpha}=\frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}}\,, \qquad (9.27)$$

$$\lambda_{\mathcal{G}}^{\alpha}=-\lambda_{\mathcal{TG}}^{\alpha}\,, \qquad (9.28)$$

and

$$\lambda_{\mathcal{M}}^{\alpha}=\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}}+\lambda_{\mathcal{TG}}^{\alpha}\theta^{\overline{\overline{\alpha}}}\psi^{\overline{\alpha}}-\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)\,. \qquad (9.29)$$

Thus we are short a condition for specification of $\lambda_{\mathcal{TG}}^{\alpha}$. By an argument similar to that used to obtain Eq. (5.28) concerning the desirability of the additivity of the internal energy and the gravitational potential, we select

$$\lambda_{\mathcal{TG}}^{\alpha}=\lambda_{\mathcal{T}}^{\alpha}=\frac{1}{\theta^{\overline{\overline{\alpha}}}}\quad\text{for }\alpha\in\mathfrak{J}\,. \qquad (9.30)$$

Substitution of the values of the Lagrange multipliers into Eq. (9.20) yields the augmented EI

$$
\begin{aligned}
&\sum_{\alpha\in\mathfrak{J}}\mathcal{S}_*^{\overline{\overline{\alpha}}}-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathcal{E}_*^{\overline{\overline{\alpha}}}+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathbf{v}^{\overline{\alpha}}\cdot\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}\\
&\quad+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}-\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)\mathcal{M}_*^{\overline{\overline{\alpha}}}\\
&\quad-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathcal{G}_*^{\overline{\overline{\alpha}}}+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathcal{T}_*^{\overline{\overline{\alpha}}}+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. \qquad (9.31)
\end{aligned}
$$

The next steps are to insert the conservation equations into this equation, perform the manipulations needed to cancel out terms as possible, and rearrange the surviving terms into a useful force-flux form.

9.4.3 Elimination of Time Derivatives

Equation (9.31) is written in expanded form by substituting the equations from Tables 6.3 and 7.2. Because there are no common curves in the single-phase-flow system, all terms that are related to processes at a common curve can be dropped. After cancellation of the material derivative terms, as is ensured by the selection of the Lagrange multipliers, the expanded form of equation Eq. (9.31) that remains without any further rearrangement or cancellation is

$$\begin{aligned}
&\sum_{\alpha\in\mathfrak{J}}\left[\eta^{\overline{\overline{\alpha}}}\mathsf{I}{:}\mathsf{d}^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}b^{\alpha}-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{M}\,\eta^{\overline{\overline{\alpha,\kappa}}}-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{\Phi}-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}\right)\right] &&\qquad \mathcal{S}_*^{\overline{\overline{\alpha}}}\\
&-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\frac{\mathrm{D}^{\overline{\alpha}}K_E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\left[E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)\right]\mathsf{I}{:}\mathsf{d}^{\overline{\overline{\alpha}}}\right\} &&\qquad \mathcal{E}_*^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}h^{\alpha}\right) &&\qquad \mathcal{E}_*^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}}+\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}}{2}+K_E^{\overline{\overline{\alpha,\kappa}}}\right) &&\qquad \mathcal{E}_*^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{Q}\right] &&\qquad \mathcal{E}_*^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathsf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right) &&\qquad \mathcal{E}_*^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathbf{v}^{\overline{\alpha}}\cdot\left[\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathsf{I}{:}\mathsf{d}^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{M}\,\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\right] &&\qquad \mathcal{P}_*^{\overline{\overline{\alpha}}}\\
&-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathbf{v}^{\overline{\alpha}}\cdot\overset{\kappa\to\alpha}{\mathbf{T}}-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathbf{v}^{\overline{\alpha}}\cdot\left[\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathsf{t}^{\overline{\overline{\alpha}}}\right)\right] &&\qquad \mathcal{P}_*^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}-\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathsf{I}{:}\mathsf{d}^{\overline{\overline{\alpha}}}-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{M}\right)\right] &&\qquad \mathcal{M}_*^{\overline{\overline{\alpha}}}\\
&-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\Psi^{\overline{\overline{\alpha}}}\mathsf{I}{:}\mathsf{d}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}\right] &&\qquad \mathcal{G}_*^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\overset{\kappa\to\alpha}{M}\,\psi^{\overline{\overline{\alpha,\kappa}}}+\overset{\kappa\to\alpha}{G}+\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}\right)\right] &&\qquad \mathcal{G}_*^{\overline{\overline{\alpha}}}
\end{aligned}$$

$$+ \sum_{\alpha\in\mathfrak{J}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\langle \rho_\alpha \left[\frac{\partial^{(n)}\psi_\alpha}{\partial t} + \mathbf{v}_\alpha\cdot \left(\mathsf{I} - \mathsf{I}_\alpha^{(n)}\right) \cdot\mathbf{g}_\alpha \right] \right\rangle_{\Omega_\alpha,\Omega} \qquad \mathcal{G}_*^{\overline{\overline{\alpha}}}$$

$$+ \frac{1}{\theta^{\overline{\overline{w}}}} \left\langle \mathbf{n}_w\cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right) p_w \right\rangle_{\Omega_{ws},\Omega} \qquad \mathcal{T}_*^{\overline{\overline{w}}}$$

$$+ \frac{1}{\theta^{\overline{\overline{w}}}} \left[\left\langle \eta_w \frac{\mathrm{D}^{\overline{s}}(\theta_w - \theta^{\overline{\overline{w}}})}{\mathrm{D}t} \right\rangle_{\Omega_w,\Omega} + \left\langle \rho_w \frac{\mathrm{D}^{\overline{s}}\left(\mu_w - \mu^{\overline{w}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_w,\Omega} \right] \qquad \mathcal{T}_*^{\overline{\overline{w}}}$$

$$- \frac{1}{\theta^{\overline{\overline{w}}}} \left[\eta^{\overline{\overline{w}}} \nabla\theta^{\overline{\overline{w}}} - \nabla(\varepsilon^{\overline{\overline{w}}} p^w) + \varepsilon^{\overline{\overline{w}}} \rho^w \nabla\mu^{\overline{w}} \right] \cdot \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) \qquad \mathcal{T}_*^{\overline{\overline{w}}}$$

$$- \frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot (\mathbf{v}_{ws} - \mathbf{v}_s)\, \boldsymbol{\sigma}_s : \frac{\mathsf{C}_s}{j_s} \right\rangle_{\Omega_{ws},\Omega} \qquad \mathcal{T}_*^{\overline{\overline{s}}}$$

$$- \frac{1}{\theta^{\overline{\overline{s}}}} \left[\left\langle \mathbf{n}_s\cdot\mathsf{t}_s\cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_{ws},\Omega} - \left\langle \eta_s \frac{\mathrm{D}^{\overline{s}}(\theta_s - \theta^{\overline{\overline{s}}})}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} \right] \qquad \mathcal{T}_*^{\overline{\overline{s}}}$$

$$+ \frac{1}{\theta^{\overline{\overline{s}}}} \left[\left\langle \rho_s \frac{\mathrm{D}^{\overline{s}}(\mu_s - \mu^{\overline{s}})}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} - \nabla\cdot \left\langle \left[\mathsf{t}_s - \boldsymbol{\sigma}_s : \frac{\mathsf{C}_s}{j_s} \mathsf{I} \right] \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_s,\Omega} \right] \qquad \mathcal{T}_*^{\overline{\overline{s}}}$$

$$- \frac{1}{\theta^{\overline{\overline{s}}}} \left[\varepsilon^{\overline{\overline{s}}} \mathsf{t}^s : \mathsf{d}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}} \boldsymbol{\sigma}^{\overline{\overline{s}}} : \frac{\mathsf{C}^s}{j^s} \mathsf{I} : \mathsf{d}^{\overline{\overline{s}}} - \left\langle \left(\nabla\cdot\mathsf{t}_s - \nabla\boldsymbol{\sigma}_s : \frac{\mathsf{C}_s}{j_s} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right) \right\rangle_{\Omega_s,\Omega} \right] \qquad \mathcal{T}_*^{\overline{\overline{s}}}$$

$$+ \frac{1}{\theta^{\overline{\overline{ws}}}} \left[\left\langle \eta_{ws} \frac{\mathrm{D}'^{\overline{s}}(\theta_{ws} - \theta^{\overline{\overline{ws}}})}{\mathrm{D}t} \right\rangle_{\Omega_{ws},\Omega} + \left\langle \rho_{ws} \frac{\mathrm{D}'^{\overline{s}}(\mu_{ws} - \mu^{\overline{ws}})}{\mathrm{D}t} \right\rangle_{\Omega_{ws},\Omega} \right] \qquad \mathcal{T}_*^{\overline{\overline{ws}}}$$

$$- \frac{1}{\theta^{\overline{\overline{ws}}}} \left[\eta^{\overline{\overline{ws}}} \nabla\theta^{\overline{\overline{ws}}} + \nabla\cdot \left\langle \mathsf{I}'_{ws} \gamma_{ws} \right\rangle_{\Omega_{ws},\Omega} + \varepsilon^{\overline{\overline{ws}}} \rho^{ws} \nabla\mu^{\overline{ws}} \right] \cdot \left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \qquad \mathcal{T}_*^{\overline{\overline{ws}}}$$

$$+ \frac{1}{\theta^{\overline{\overline{ws}}}} \left[\nabla\cdot \left\langle \left(\mathsf{I} - \mathsf{I}'_{ws}\right) \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{ws}}\right) \gamma_{ws} \right\rangle_{\Omega_{ws},\Omega} + \left\langle \left(\mathsf{I} - \mathsf{I}'_{ws}\right) \gamma_{ws} \right\rangle_{\Omega_{ws},\Omega} : \mathsf{d}^{\overline{\overline{ws}}} \right] \qquad \mathcal{T}_*^{\overline{\overline{ws}}}$$

$$+ \frac{1}{\theta^{\overline{\overline{ws}}}} \left\langle \nabla'\cdot\mathsf{I}'_{ws}\cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right) \gamma_{ws} \right\rangle_{\Omega_{ws},\Omega} \qquad \mathcal{T}_*^{\overline{\overline{ws}}}$$

$$+ \frac{1}{\theta^{\overline{\overline{ws}}}} \left\langle \eta_{ws} \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_{ws}\right) \right\rangle_{\Omega_{ws},\Omega} \cdot\nabla\theta^{\overline{\overline{ws}}} \qquad \mathcal{T}_*^{\overline{\overline{ws}}}$$

$$+ \frac{1}{\theta^{\overline{\overline{ws}}}} \left\langle \rho_{ws} \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_{ws}\right) \right\rangle_{\Omega_{ws},\Omega} \cdot\nabla\mu^{\overline{ws}} \qquad \mathcal{T}_*^{\overline{\overline{ws}}}$$

$$- \frac{1}{\theta^{\overline{\overline{w}}}} \left[\left\langle \rho_w \frac{\mathrm{D}^{\overline{s}}\psi^{\overline{w}}}{\mathrm{D}t} \right\rangle_{\Omega_w,\Omega} + \varepsilon^{\overline{\overline{w}}} \rho^w \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) \cdot\nabla\psi^{\overline{w}} \right] \qquad \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{w}}}$$

$$- \frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \rho_s \frac{\mathrm{D}^{\overline{s}}\psi^{\overline{s}}}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega} \qquad \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{s}}}$$

$$- \frac{1}{\theta^{\overline{\overline{ws}}}} \left[\left\langle \rho_{ws} \frac{\mathrm{D}'^{\overline{s}}\psi^{\overline{ws}}}{\mathrm{D}t} \right\rangle_{\Omega_{ws},\Omega} + \varepsilon^{\overline{\overline{ws}}} \rho^{ws} \nabla\psi^{\overline{ws}}\cdot \left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \right] \qquad \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$$

$$\begin{aligned}
&+ \frac{1}{\theta^{\overline{\overline{ws}}}} \left\langle \rho_{ws} \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\mathbf{l} - \mathbf{l}'_{ws} \right) \right\rangle_{\Omega_{ws},\Omega} \cdot \nabla \psi^{\overline{ws}} && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}} \\
&= \sum_{\alpha \in \mathfrak{J}} \Lambda^{\overline{\overline{\alpha}}} \geq 0 \,. && \mathcal{S}_{**}^{\overline{\overline{\alpha}}}
\end{aligned} \tag{9.32}$$

In this equation, the identification of an equation at the right side indicates the particular balance, conservation, or thermodynamic relation that provided the terms appearing in the line.

This equation is obviously very long, and would be much longer if the summations over the entities were expanded out. Some of these summations can be retained at this point because the notation introduced in Chap. 6 allows the statement of the conservation equations to be independent of the entity. Because the thermodynamic expressions developed in Chap. 7 are of different forms for fluids, solids, and interfaces, these expressions are introduced explicitly into the equation. The next step to be employed is mathematical manipulation of Eq. (9.32) to cancel out and recombine appropriate terms into a form that is useful for obtaining closure relations.

9.4.4 Manipulation Insights

The manipulations required to develop Eq. (9.32) toward force-flux form are somewhat daunting, primarily because of the number of operations needed rather than their complexity. Admittedly, keeping the entity qualifiers, overbars, and vector products straight requires meticulous and cautious bookkeeping. The main technical issue that one encounters is deciding which combinations of terms are in a useful form and which require further rearrangement. Often this decision can only be made following false starts that lead nowhere and are reconsidered. The steps we have followed are outlined briefly here and in more detail in Sect. C.1 of Appendix C. At this point, we present a few "tricks" that are employed but which may not be obvious. These are motivated by insights gained in revising Eq. (9.32). Some additional comments concerning motivation for combination of various terms will be postponed to the next subsection. In the present section, some exact manipulations are presented.

Inter-entity entropy transfer

The summation of the entropy equations for the three entities appears at the beginning of Eq. (9.32) and contains terms involving the transfer of entropy between entities due to phase change and non-advective processes. The net transfer within the system must be zero, since entropy generation is accounted for by the $\Lambda^{\overline{\overline{\alpha}}}$ terms associated with the entities. Therefore, we can state

$$\sum_{\alpha\in\mathfrak{I}}\left(\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\overset{\kappa\to\alpha}{M}\,\overline{\eta}^{\overline{\overline{\alpha,\kappa}}}+\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\overset{\kappa\to\alpha}{\Phi}\right)=0\,. \tag{9.33}$$

Material derivative of $K_E^{\overline{\overline{ws}}}$

The material derivative of $K_E^{\overline{\overline{ws}}}$ is expressed using the velocity of the *ws* interface. It will be useful to express this in terms of the average of a material derivative on the surface. This is accomplished by first invoking the identity

$$\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\frac{\mathrm{D}^{\overline{ws}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t}=\left\langle\rho_{ws}\frac{\mathrm{D}^{\overline{ws}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega}\,. \tag{9.34}$$

The definition of the material derivative on the surface, Eq. (7.84), is then introduced based on identity Eq. (7.85). After macroscale quantities are pulled out of the averaging operator, the result is

$$\begin{aligned}\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\frac{\mathrm{D}^{\overline{ws}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t}=&\left\langle\rho_{ws}\frac{\mathrm{D}'^{\overline{s}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega}+\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\cdot\nabla K_E^{\overline{\overline{ws}}}\\&-\left\langle\rho_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}'_{ws}\right)\cdot\nabla K_E^{\overline{\overline{ws}}}\right\rangle_{\Omega_{ws},\Omega}\,.\end{aligned} \tag{9.35}$$

Inter-entity mass exchange

Inter-entity mass exchange terms arise in all the conservation equations. The combination of these terms across equation sources is undertaken for the purpose of obtaining expressions involving the mass exchange flux multiplied by some force that drives the exchange, such as a difference in chemical potentials.

As an example of manipulations that are needed, consider the terms involving mass exchange multiplied by velocity squared that arises in Eq. (9.32). Extraction of the three terms that involve inter-entity mass exchange multiplied by some velocity squared yields the terms we will designate as M_v where

$$\begin{aligned}M_v=&\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left(\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}}{2}\right)-\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left(\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\right)\\&+\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\right)\,.\end{aligned} \tag{9.36}$$

These summations may be combined to obtain

$$M_v=\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left[\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\right)}{2}\right]\,. \tag{9.37}$$

In the derivation of equations for porous medium flow, it is appropriate to express all the velocities in an objective form, relative to the velocity of the solid phase. We can subtract and add $\mathbf{v}^{\overline{s}}$ to each term in parentheses in Eq. (9.37) such that the velocities are each relative to this velocity. Expansion of the resulting expression then gives

$$
\begin{aligned}
M_v = & \sum_{\alpha\in\mathfrak{I}} \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}} \overset{\kappa\to\alpha}{M} \left[\frac{(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}) \cdot (\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}})}{2} \right] \\
& - \sum_{\alpha\in\mathfrak{I}} \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}} \overset{\kappa\to\alpha}{M} \left[(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}) \cdot (\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}} - \mathbf{v}^{\overline{s}}) \right] \\
& + \sum_{\alpha\in\mathfrak{I}} \sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}} \frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}} \overset{\kappa\to\alpha}{M} \left[\frac{(\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}} - \mathbf{v}^{\overline{s}}) \cdot (\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}} - \mathbf{v}^{\overline{s}})}{2} \right] .
\end{aligned}
\tag{9.38}
$$

Expansion of the summations over the entities ($\mathfrak{I} = \{w,s,ws\}$) and the connected entities ($\mathfrak{I}_{\mathrm{cw}} = \{ws\}$, $\mathfrak{I}_{\mathrm{cs}} = \{ws\}$, and $\mathfrak{I}_{\mathrm{cws}} = \{w,s\}$) subject to the definition of $\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}}$ given in Eq. (6.96), followed by rearrangement of the result gives

$$
\begin{aligned}
M_v = & \left(\frac{1}{\theta^{\overline{\overline{\overline{w}}}}} - \frac{1}{\theta^{\overline{\overline{\overline{ws}}}}} \right) \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\frac{\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} \right) \overset{ws\to w}{M} \\
& + \left(\frac{1}{\theta^{\overline{\overline{\overline{s}}}}} - \frac{1}{\theta^{\overline{\overline{\overline{ws}}}}} \right) \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \cdot \left(\frac{\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} \right) \overset{ws\to s}{M} \\
& + \frac{1}{\theta^{\overline{\overline{\overline{w}}}}} \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}} \right) \cdot \left[\left(\frac{\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}}{2} \right) - \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \right] \overset{ws\to w}{M} \\
& - \frac{1}{\theta^{\overline{\overline{\overline{ws}}}}} \left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \cdot \left\{ \left[\left(\frac{\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} \right) - \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \right] \overset{ws\to w}{M} \right. \\
& \left. + \left[\left(\frac{\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} \right) - \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right) \right] \overset{ws\to s}{M} \right\} .
\end{aligned}
\tag{9.39}
$$

This combination of terms will appear subsequently in the full algebraic rearrangement of Eq. (9.32). Combination and rearrangement of other inter-entity exchange terms are also needed, but these will not be detailed here since they are similar to, though less complex than, the previous derivation.

Solid-phase stress tensor

The solid-phase stress tensor integrated over the boundary of the surface is rearranged so that the normal component can be separated from the rest of the tensor. First, the unit tensor is introduced to establish the equality

$$
\left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} = \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{l} \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} . \tag{9.40}
$$

On the solid boundary, the unit tensor may be decomposed with

$$\mathsf{I} = \mathbf{n}_s\mathbf{n}_s + \mathsf{I}'_{ws} \quad \text{for } \mathbf{x} \in \Omega_{ws} \,. \tag{9.41}$$

Substitution of this relation into Eq. (9.40) then gives

$$\begin{aligned}\left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} =& \left\langle (\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s)\mathbf{n}_s \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} \\ &+ \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathsf{I}'_{ws} \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} \,.\end{aligned} \tag{9.42}$$

This equation will prove useful when forming the force-flux form of the EI.

Final comment on algebraic manipulations

The full array of mathematical manipulations is more extensive than those provided in this subsection. However, the flavor of the manipulations is the same. We use the product rule in rearranging divergence terms; relate all velocities to the solid-phase velocity by addition to and subtraction from various terms; cancel out terms that are identical; and group terms that are similar. The task can be completed after expansion of the summations and recombination back into sums. The manipulations are carried out in additional detail in Sect. C.1, and the resulting EI is provided in the next subsection.

9.4.5 Formulation of the CEI

Because the derivation of the CEI from Eq. (9.32) is a lengthy process that requires significant manipulations, it can be off-putting. However, the CEI is a key equation. It is an inequality in which the terms are arranged as a product of forces and fluxes with the requirement that its derivation be exact. No additional restrictions or approximations are employed in deriving the CEI from Eq. (9.32). In the end, it is not possible to obtain a CEI that contains only macroscopic force-flux pairings. The terms that do not satisfy this form have to be dealt with later in simplifying the CEI to an SEI, as indicated in Fig. 9.1.

The goal of this subsection is to outline the manipulations that are involved in deriving the CEI. This is provided as an aid to understanding and with the intention that it will assist an interested individual in deriving a CEI for a case not covered in this text. The results in this section follow from the rearrangement of Eq. (9.32) as outlined in Sect. C.1. We note that terms involving the entropy source, the energy source, and the remaining material derivative terms are grouped together. Similarly, terms involving the entropy flux and heat flux are grouped together after application of the product rule; a work term from the solid-phase thermodynamics is grouped together with the solid-phase heat flux vector terms because it is of a similar form. The macroscale equilibrium conditions given in Sect. 7.8.1 are used to guide the formulation of the CEI because the conditions obtained suggest forces or fluxes that will be zero at equilibrium.

Table 9.1 CEI formulation summary for the derivation of Eq. (9.43), where the operation abbreviations are A for addition and subtraction, E for Euler equation identity, I for identity tensor components as shown in Eq. (9.41), O for objective form, and P for the product rule. The general entity qualifier α implies all entities unless otherwise noted

Line(s)	Force	Precursor Equation(s)	Operations
1–4	—	$\mathcal{S}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$	O,A
5–6	—	$\mathcal{S}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{s}}}$	P
7–8	$\mathbf{d}^{\overline{\overline{\alpha}}}$	$\mathcal{S}_*^{\overline{\overline{\alpha}}}, \mathcal{M}_*^{\overline{\overline{\alpha}}}, \boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{s}}}, \mathcal{T}_*^{\overline{\overline{ws}}}$	E,P
9–10	$\nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)$	$\mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{s}}}$	P
11	$\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{w}}+K_E^{\overline{\overline{w}}}+\psi^{\overline{w}}\right)$ $-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)$	$\mathcal{M}_*^{\overline{\overline{w}}}, \mathcal{M}_*^{\overline{\overline{ws}}}$	—
12	$\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{s}}+K_E^{\overline{\overline{s}}}+\psi^{\overline{s}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^s}{3\rho^s j^s}\right)$ $-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)$	$\mathcal{M}_*^{\overline{\overline{s}}}, \mathcal{M}_*^{\overline{\overline{ws}}}$	A
13	—	$\mathcal{T}_*^{\overline{\overline{s}}}$	A,I
14–16	$\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}$	$\mathcal{M}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{w}}},\ \alpha \in \{w, ws\}$	O
17–19	$\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}$	$\mathcal{M}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{s}}},\ \alpha \in \{s, ws\}$	A,O
20–21	$\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}$	$\mathcal{M}_*^{\overline{\overline{w}}}, \boldsymbol{\mathcal{P}}_*^{\overline{\overline{w}}}, \mathcal{E}_*^{\overline{\overline{w}}}, \mathcal{G}_*^{\overline{\overline{w}}}, \mathcal{T}_*^{\overline{\overline{w}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{w}}}$	A,O
22–26	$\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}$	$\mathcal{M}_*^{\overline{\overline{ws}}}, \boldsymbol{\mathcal{P}}_*^{\overline{\overline{ws}}}, \mathcal{E}_*^{\overline{\overline{ws}}}, \mathcal{G}_*^{\overline{\overline{ws}}}, \mathcal{T}_*^{\overline{\overline{ws}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$	A,O
27–28	—	$\mathcal{G}_*^{\overline{\overline{ws}}}, \mathcal{T}_*^{\overline{\overline{\alpha}}}$	A,I
29	—	$\mathcal{T}_*^{\overline{\overline{s}}}$	I
30	—	$\mathcal{T}_*^{\overline{\overline{s}}}$	—
31	—	$\mathcal{T}_*^{\overline{\overline{ws}}}$	A
32	—	$\mathcal{T}_*^{\overline{\overline{ws}}}$	—
33	—	$\mathcal{E}_*^{\overline{\overline{ws}}}, \mathcal{T}_*^{\overline{\overline{ws}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$	A,O
34	—	$\mathcal{S}_*^{\overline{\overline{\alpha}}}$	—

Providing a comprehensive derivation with incremental results is not practical as part of the flow of this text. Thus, as a compromise between exhaustive detail and simply writing the result, we provide comprehensive guidance for the rearrangements needed in deriving the CEI of Eq. (9.43) in Sect. C.1 and summarize that guidance in Table 9.1. The "Lines" column in the table refers to the line numbers in

Eq. (9.43). The "Precursor Equation(s)" contribute terms to the CEI lines. Because the elements of the precursor equations are identified in Eq. (9.32), some guidance exists as to where the terms associated with a particular line of the CEI arise. The "Operations" column lists the type of manipulations needed to derive the final form of the indicated lines from precursor expressions. A significant component of the CEI derivation involves collecting terms that have a common multiplier or which cancel. Also, terms are often added in and then subtracted out to produce a desirable form (denoted as an "A" operation), as has been encountered in deriving Eq. (9.38) from Eq. (9.37) by adding and subtracting $\mathbf{v}^{\overline{s}}$. The Euler equations for entities from Table 7.1 are employed at various times ("E" operations); the identity tensor is divided into components as shown in Eq. (9.41) ("I" operations); expressions are put in objective form by referencing all velocities to the solid-phase velocity as demonstrated in Eqs. (9.35) and (9.39) ("O" operations); and the product rule is used ("P" operations). Terms that end up in a particular line of the CEI originate from the various precursor conservation and thermodynamic equations that were employed in forming the augmented EI. The list of precursor equations and operations needed to derive a particular line or group of lines of Eq. (9.43) is an indicator of the type and extent of manipulations needed. It is emphasized that the manipulations performed are guided by the desire to arrange the CEI in a force-flux form to the extent possible without introducing approximations.

Performing the manipulations summarized in Table 9.1 results in the macroscale CEI for single-fluid-phase flow in a porous medium as

$$-\sum_{\alpha\in\mathfrak{J}_\mathrm{P}} \left\{ \varepsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}} \left[\varepsilon^{\overline{\overline{\alpha}}} h^{\alpha} + \left\langle \eta_\alpha \frac{\mathrm{D}^{\overline{s}}\left(\theta_\alpha - \theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} \right.\right. \qquad 1$$

$$\left.\left. + \left\langle \rho_\alpha \frac{\mathrm{D}^{\overline{s}}\left(\mu_\alpha + \psi_\alpha - \mu^{\overline{\alpha}} - K_E^{\overline{\overline{\alpha}}} - \psi^{\overline{\alpha}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega} \right]\right\} \qquad 2$$

$$-\left\{ \varepsilon^{\overline{\overline{ws}}} b^{ws} - \frac{1}{\theta^{\overline{\overline{\overline{ws}}}}} \left[\varepsilon^{\overline{\overline{ws}}} h^{ws} + \left\langle \eta_{ws} \frac{\mathrm{D}'^{\overline{s}}\left(\theta_{ws} - \theta^{\overline{\overline{ws}}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_{ws},\Omega} \right.\right. \qquad 3$$

$$\left.\left. + \left\langle \rho_{ws} \frac{\mathrm{D}'^{\overline{s}}\left(\mu_{ws} + \psi_{ws} - \mu^{\overline{ws}} - K_E^{\overline{\overline{ws}}} - \psi^{\overline{ws}}\right)}{\mathrm{D}t} \right\rangle_{\Omega_{ws},\Omega} \right]\right\} \qquad 4$$

$$-\sum_{\alpha\in\mathfrak{J}_{/S}} \nabla\cdot \left[\varepsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}} - \frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}} \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_\mathbf{g}^{\overline{\overline{\alpha}}} \right) \right] \qquad 5$$

$$-\nabla\cdot \left\{ \varepsilon^{\overline{\overline{s}}} \boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{\overline{s}}}}} \left[\varepsilon^{\overline{\overline{s}}} \mathbf{q}^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{s}}} \mathbf{q}_\mathbf{g}^{\overline{\overline{s}}} - \left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s,\Omega} \right] \right\} \qquad 6$$

$$+\frac{1}{\theta^{\overline{\overline{\overline{w}}}}} \left(\varepsilon^{\overline{\overline{w}}} \mathbf{t}^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{w}}} p^{w} \mathbf{I} \right) {:} \mathbf{d}^{\overline{\overline{w}}} + \frac{1}{\theta^{\overline{\overline{\overline{s}}}}} \left(\varepsilon^{\overline{\overline{s}}} \mathbf{t}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}} \mathbf{t}^{s} \right) {:} \mathbf{d}^{\overline{\overline{s}}} \qquad 7$$

$$+\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left[\varepsilon^{\overline{ws}}\mathsf{t}^{\overline{\overline{ws}}}-\varepsilon^{\overline{ws}}\gamma^{ws}\mathsf{I}+\left\langle\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}\right]:\mathsf{d}^{\overline{\overline{ws}}} \qquad 8$$

$$-\sum_{\alpha\in\mathfrak{I}_{/S}}\left(\varepsilon^{\overline{\alpha}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\alpha}}\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}\right)\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\right) \qquad 9$$

$$-\left[\varepsilon^{\overline{s}}\mathbf{q}^{\overline{\overline{s}}}+\varepsilon^{\overline{s}}\mathbf{q}_{\mathbf{g}}^{\overline{\overline{s}}}-\left\langle\left(\mathsf{t}_s-\frac{\boldsymbol{\sigma}_s:\mathsf{C}_s}{j_s}\mathsf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\right) \qquad 10$$

$$+\overset{w\rightarrow ws}{M}\left[\frac{1}{\theta^{\overline{\overline{\overline{w}}}}}\left(\mu^{\overline{w}}+K_E^{\overline{\overline{w}}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\right] \qquad 11$$

$$+\overset{s\rightarrow ws}{M}\left[\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left(\mu^{\overline{s}}+K_E^{\overline{\overline{s}}}+\psi^{\overline{s}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathsf{C}^s}{3\rho^s j^s}\right)-\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\right] \qquad 12$$

$$+\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left\langle\left(\frac{\boldsymbol{\sigma}_s:\mathsf{C}_s}{\rho_s j_s}-\frac{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s}{\rho_s}-\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathsf{C}^s}{3\rho^s j^s}\right)\rho_s\left(\mathbf{v}_s-\mathbf{v}_{ws}\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega} \qquad 13$$

$$-\left\{\overset{w\rightarrow ws}{Q}+\overset{w\rightarrow ws}{G}+\left(\overline{E}_w^{\overline{ws}}+K_{Ew}^{\overline{\overline{ws}}}+\psi_w^{\overline{ws}}\right)\overset{w\rightarrow ws}{M}\right. \qquad 14$$

$$+\left[\overset{w\rightarrow ws}{\mathbf{T}}+\frac{\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{w\rightarrow ws}{M}\right]\cdot\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right) \qquad 15$$

$$\left.-\left\langle\mathbf{n}_w\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)p_w\right\rangle_{\Omega_{ws},\Omega}\right\}\left(\frac{1}{\theta^{\overline{\overline{\overline{w}}}}}-\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\right) \qquad 16$$

$$-\left\{\overset{s\rightarrow ws}{Q}+\overset{s\rightarrow ws}{G}+\left(\overline{E}_s^{\overline{ws}}+K_{Es}^{\overline{\overline{ws}}}+\psi_s^{\overline{ws}}\right)\overset{s\rightarrow ws}{M}\right. \qquad 17$$

$$+\left[\overset{s\rightarrow ws}{\mathbf{T}}+\frac{\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{s\rightarrow ws}{M}\right]\cdot\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right) \qquad 18$$

$$\left.+\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega}\right\}\left(\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}-\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\right) \qquad 19$$

$$-\frac{1}{\theta^{\overline{\overline{\overline{w}}}}}\left\{\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}}-\nabla\left(\varepsilon^{\overline{w}}p^w\right)+\varepsilon^{\overline{w}}\rho^w\nabla\left(\mu^{\overline{w}}+K_E^{\overline{\overline{w}}}+\psi^{\overline{w}}\right)+\varepsilon^{\overline{w}}\rho^w\mathbf{g}^{\overline{w}}\right. \qquad 20$$

$$\left.-\left[\overset{w\rightarrow ws}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{w\rightarrow ws}{M}+\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\overset{w\rightarrow ws}{M}\right]\right\}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right) \qquad 21$$

$$-\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left\{\eta^{\overline{\overline{ws}}}\nabla\theta^{\overline{\overline{ws}}}+\nabla\cdot\left\langle\mathsf{I}'_{ws}\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}+\varepsilon^{\overline{ws}}\rho^{ws}\nabla\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\right. \qquad 22$$

$$+\varepsilon^{\overline{ws}}\rho^{ws}\mathbf{g}^{\overline{ws}}+\overset{w\rightarrow ws}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{w\rightarrow ws}{M}+\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\overset{w\rightarrow ws}{M} \qquad 23$$

$$+\overset{s\rightarrow ws}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{s\rightarrow ws}{M}+\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\overset{s\rightarrow ws}{M} \qquad 24$$

$$
\begin{aligned}
&\qquad -\Big\langle \eta_{ws}\left(\mathbf{I}-\mathbf{I}'_{ws}\right)\Big\rangle_{\Omega_{ws},\Omega}\cdot\nabla\theta^{\overline{\overline{ws}}} && 25\\
&\qquad -\Big\langle \rho_{ws}\left(\mathbf{I}-\mathbf{I}'_{ws}\right)\Big\rangle_{\Omega_{ws},\Omega}\cdot\nabla\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\Bigg\}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right) && 26\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\Big\langle\Big[p_w\mathbf{n}_w-\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s+\gamma_{ws}\left(\nabla'\cdot\mathbf{I}'_{ws}\right) && 27\\
&\qquad\qquad +\rho_{ws}\mathbf{g}_{ws}\cdot\left(\mathbf{I}-\mathbf{I}'_{ws}\right)\Big]\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{ws},\Omega} && 28\\
&-\frac{1}{\theta^{\overline{\overline{s}}}}\Big\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'_{ws}\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_{ws},\Omega} && 29\\
&+\frac{1}{\theta^{\overline{\overline{s}}}}\Big\langle\left(\nabla\cdot\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s:\frac{\mathsf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\Big\rangle_{\Omega_s,\Omega} && 30\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\Big\langle\eta_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{ws}\right)\Big\rangle_{\Omega_{ws},\Omega}\cdot\nabla\theta^{\overline{\overline{ws}}} && 31\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\nabla\cdot\Big\langle\left(\mathbf{I}-\mathbf{I}'_{ws}\right)\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}}\right)\gamma_{ws}\Big\rangle_{\Omega_{ws},\Omega} && 32\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\Big\langle\rho_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{ws}\right)\Big\rangle_{\Omega_{ws},\Omega}\cdot\nabla\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right) && 33\\
&=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. && 34
\end{aligned}
\tag{9.43}
$$

Many of the lines in this equation are in the form of a macroscopic flux multiplying a macroscopic force where both factors are zero at equilibrium (e.g., lines 7–12). However other lines still contain the averaging operator applied to microscale quantities (e.g., lines 13, 19, and 30), while others are averages of microscopic force-flux products (e.g., lines 27–28). To be able to utilize Eq. (9.43) as a guide to closure relations, it is necessary to make some approximations. We continue to emphasize that the CEI given in Eq. (9.43) does not employ any approximations beyond those inherent in constraining the EI with conservation and thermodynamic relations. Thus, if subsequent utilization of relations developed by imposing approximations shows them to be inadequate, one can return to this CEI and consider alternative approximations. In the following section, we will make a series of approximations that are reasonable for many applications and thereby simplify the CEI to an SEI.

9.5 Simplified Entropy Inequality

The SEI is the second key archival equation in TCAT analysis. The SEI for a macroscale analysis is always arranged in strict force-flux form where each force and flux is a macroscale quantity. Thus, the SEI is an essential component in formulating closed, solvable TCAT models in that it guides the formulation of closure relations.

The development of the SEI for macroscale models parallels the development of the SEI for a microscale system as described in Sect. 5.5.

Because the CEI is a final exact form of the EI but is not in strict macroscale force-flux form, two general types of additional manipulations are employed to derive an SEI. First, mathematical approximations, referred to as SEI approximations,, motivated by expected system dynamics are employed so that terms in the CEI contribute to the desired force-flux form. Second, the particular system of interest is restricted to be some subset of the general single-fluid-phase system defined according to the three primary restrictions listed in Sect. 9.2. This is accomplished by the use of secondary restrictions. Many combinations of secondary restrictions and SEI approximations exist. Therefore, a single CEI can be mapped to a set of possible SEI's corresponding to different systems. This is why both the SEI and the CEI are of important archival value for TCAT model development. A representative set of SEI approximations and secondary restrictions will be stated formally to highlight their utilization in TCAT model development.

9.5.1 The Need for Approximations

We emphasize that the approximations to be proposed here are subject to change as new insights develop or if the system of interest behaves in a way that is not consistent with the approximations. The mathematical approximations are always subject to validation based on some mix of mathematical analysis, computer simulation, laboratory experimentation, and field studies. When a system satisfies the primary restrictions proposed but the TCAT model does not adequately describe the system, the logical entry point for reanalysis of the system is the set of SEI approximations.

The need for additional manipulations to derive an SEI from the CEI of Eq. (9.43) can be deduced from a cursory examination of Table 9.1. The table indicates that a force-flux form is not obtained in lines 1–6, 13, and 27–33 of the equation. Thus, work on these lines is needed to develop an SEI that consists exclusively of force-flux pairs. Examination of the terms in the equation components of these lines will suggest appropriate SEI approximations and secondary restrictions. These will be of two types. One involves elimination of groups of terms by approximating them to be much smaller than other terms in the equation. The other is based on approximations that allow averages of groups of terms to be approximated in terms of macroscale variables.

9.5.2 Elimination of Terms

Lines 1–6 in Eq. (9.43) are not in force-flux form. However, these lines have been arranged in convenient groupings. Elimination of these lines of the CEI will be enabled by the following SEI approximation:

SEI Approximation 9.1 (Macroscopically Simple System)
The system of concern is macroscopically simple, such that the entropy source is balanced by the sum of a heat source and deviation terms with

$$\varepsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left[\varepsilon^{\overline{\overline{\alpha}}} h^{\alpha} + \left\langle \eta_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\theta_{\alpha} - \theta^{\overline{\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \right. \\ \left. + \left\langle \rho_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{\alpha} + \psi_{\alpha} - \mu^{\overline{\alpha}} - K_E^{\overline{\overline{\alpha}}} - \psi^{\overline{\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \right] = 0 \quad \textit{for } \alpha \in \{w, s\} \tag{9.44}$$

and

$$\varepsilon^{\overline{\overline{ws}}} b^{ws} - \frac{1}{\theta^{\overline{\overline{ws}}}} \left[\varepsilon^{\overline{\overline{ws}}} h^{ws} + \left\langle \eta_{ws} \frac{\mathrm{D}'^{\overline{s}} \left(\theta_{ws} - \theta^{\overline{ws}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{ws},\Omega} \right. \\ \left. + \left\langle \rho_{ws} \frac{\mathrm{D}'^{\overline{s}} \left(\mu_{ws} + \psi_{ws} - \mu^{\overline{ws}} - K_E^{\overline{\overline{ws}}} - \psi^{\overline{ws}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{ws},\Omega} \right] = 0\,; \tag{9.45}$$

and the entropy flux is balanced by a non-advective energy flux for all entities, consisting of heat and mechanical contributions, such that

$$\varepsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}} - \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}} \right) = \mathbf{0} \quad \textit{for } \alpha \in \{w, ws\} \tag{9.46}$$

and

$$\varepsilon^{\overline{\overline{s}}} \boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{s}}}} \left[\varepsilon^{\overline{\overline{s}}} \mathbf{q}^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{s}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{s}}} - \left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s,\Omega} \right] = \mathbf{0}\,. \tag{9.47}$$

This SEI approximation is reasonable because like terms have been paired—entropy sources with energy sources and entropy fluxes with energy fluxes. The deviation terms involving material derivatives, the vectors $\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}$, and the last term on the left side of Eq. (9.47) all originate in the averaging of the conservation and thermodynamic equations to the macroscale. When the variability of functions over the macroscale is small, these terms are negligible.

Next, consider lines 29–30 in Eq. (9.43). Each of these lines involves the average of a product of terms wherein each factor vanishes at equilibrium.[2] The product of the microscale solid-phase shear stress and the difference between the microscale lateral solid surface velocity and the average solid velocity is averaged over the solid surface in line 29. The average of this product is small relative to other terms in the

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[2] See the equilibrium conditions given by Eqs. (4.54) and (4.106).

entropy inequality. Line 30 involves an average over the solid phase of the product of a quantity that is zero at equilibrium and the difference between the point solid velocity and its average. In the system being considered, both of these terms are very small such that the product can be neglected. The following SEI approximation is introduced to eliminate lines 29 and 30 and a portion of line 10 in Eq. (9.43) from further consideration:

SEI Approximation 9.2 (Solid-phase Velocity)
Expressions that involve the average of a product of the difference between the microscale and a macroscale solid-phase velocity with another term known to vanish at equilibrium are assumed to be negligible.

Lines 31–33 all involve averages of the difference between the microscale normal component of the velocity in the interface and the macroscale velocity in the interface multiplied by, essentially, an average normal direction. This difference is presumably small. Also, the terms in these lines, taken together, have some elements that are characteristic of a Gibbs-Duhem equation. For these reasons, the sum of terms in lines 31–33 of Eq. (9.43) are taken to be negligible relative to the remaining terms in the CEI. This is stated formally in the following SEI approximation:

SEI Approximation 9.3 (Interface Velocity Difference)
Expressions involving the average of the difference between the microscale normal flow velocity in a fluid-solid interface and the average normal flow of the macroscale velocity in a fluid-solid interface are negligible.

Based on this SEI approximation, lines 31–33 are dropped from the CEI.

Lastly, an approximation can be introduced that eliminates terms involving the average of the difference between the microscale solid surface stress and its average multiplied by the mass exchange at the *ws* interface. This term is negligible when the correlation between the stress differences and the mass exchange is small, if the stress at the surface is essentially constant, or if the mass exchange at the surface is negligible. The following SEI approximation is proposed

SEI Approximation 9.4 (Stress Difference and Mass Exchange)
Terms that involve a product of the microscale mass exchange between the solid phase and the ws interface and the difference between the microscale and macroscale normal solid stress at the interface can be neglected.

SEI Approximation 9.4 allows for elimination of line 13 in Eq. (9.43).

9.5.3 Approximation of Averages

The remaining SEI approximations to be employed involve breaking of the averages of products of microscale quantities into products of macroscale quantities. The need for such a protocol exists so that many of the remaining terms in Eq. (9.43) can be expressed strictly in terms of macroscale quantities. We emphasize that all approximations are subject to revisitation if they are found to be unacceptable for a system of interest. We will make use of what seem to be the most straightforward, yet theoretically plausible, approximations.

An important quantity that enters the analysis is the macroscale geometric orientation tensor for a *ws* interface, G^{ws}, previously defined in Eq. (8.13), whose definition is repeated here with alternative equivalent representations,

$$\mathsf{G}^{ws} = \langle \mathsf{G}_{ws} \rangle_{\Omega_{ws},\Omega_{ws}} = \langle \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}} = \left\langle \mathsf{I} - \mathsf{I}'_{ws} \right\rangle_{\Omega_{ws},\Omega_{ws}} . \tag{9.48}$$

Note that G_{ws} terms exist as products with the scalars η_{ws}, γ_{ws}, and ρ_s in lines 8, 25, and 26 of Eq. (9.43). Also, because $\mathsf{I}'_{ws} = \mathsf{I} - \mathsf{G}_{ws}$, the product $\mathsf{G}_{ws}\gamma_{ws}$ is seen to exist in line 22. An SEI approximation involving the average of the product of the microscale orientation tensor with a scalar facilitates evaluation of such terms and is stated:

SEI Approximation 9.5 (Geometric Orientation Products)
The average over the ws interface of a product of the microscale geometric orientation tensor G_{ws} with a microscale scalar f_{ws} can be evaluated as the product of the macroscale averages of the two components of the original expression such that

$$\langle \mathsf{G}_{ws} f_{ws} \rangle_{\Omega_{ws},\Omega} = \epsilon^{\overline{\overline{ws}}} \mathsf{G}^{ws} f^{ws} . \tag{9.49}$$

SEI Approximation 9.5 introduces no error when the interface orientation is independent of the value of the scalar involved in the product. With this approximation, and making use of the definitions of averages previously employed, the averages in lines 8, 25, and 26 of Eq. (9.43) can be evaluated with

$$\left\langle \eta_{ws} \left(\mathsf{I} - \mathsf{I}'_{ws} \right) \right\rangle_{\Omega_{ws},\Omega} = \eta^{\overline{\overline{ws}}} \mathsf{G}^{ws} , \tag{9.50}$$

$$\left\langle \left(\mathsf{I} - \mathsf{I}'_{ws} \right) \gamma_{ws} \right\rangle_{\Omega_{ws},\Omega} = \epsilon^{\overline{\overline{ws}}} \mathsf{G}^{ws} \gamma^{ws} , \tag{9.51}$$

and

$$\left\langle \rho_{ws} \left(\mathsf{I} - \mathsf{I}'_{ws} \right) \right\rangle_{\Omega_{ws},\Omega} = \epsilon^{\overline{\overline{ws}}} \rho^{ws} \mathsf{G}^{ws} . \tag{9.52}$$

The product in line 22 is similarly evaluated with

$$\left\langle \mathsf{I}'_{ws} \gamma_{ws} \right\rangle_{\Omega_{ws},\Omega} = \epsilon^{\overline{\overline{ws}}} \left(\mathsf{I} - \mathsf{G}^{ws} \right) \gamma^{ws} . \tag{9.53}$$

Kinematic equations that describe the evolution of volume, interface, and common curve densities were developed in Chap. 8 as an important element of the formulation of closed TCAT models. For a single-fluid-phase system, the evolution of the solid-phase volume fraction is described by Eq. (8.6) in the form

$$\frac{\mathrm{D}^{\overline{s}} \epsilon^{\overline{\overline{s}}}}{\mathrm{D}t} = \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{ws},\Omega} . \tag{9.54}$$

Although Eq. (9.54) is exact, lines 16, 19, 27 and 28 of Eq. (9.43) contain a product of the quantity being averaged on the right side of Eq. (9.54) with a microscale scalar that is the property of the *w* or *s* phase or of the *ws* interface. Therefore, evaluation of the averages in these lines requires an SEI approximation as follows:

SEI Approximation 9.6 (Evolution Product)
The average over the ws interface of a term involving the product of $\mathbf{n}_s \cdot (\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}})$ *with a microscale scalar can be approximated as the product of the macroscale averages of the two factors and making use of Eq. (9.54) such that*

$$\left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) f_{ws} \right\rangle_{\Omega_{ws},\Omega} = \frac{\mathrm{D}^{\bar{s}} \varepsilon^{\bar{\bar{s}}}}{\mathrm{D}t} f^{ws} \tag{9.55}$$

and

$$\left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) f_{\alpha} \right\rangle_{\Omega_{ws},\Omega} = \frac{\mathrm{D}^{\bar{s}} \varepsilon^{\bar{\bar{s}}}}{\mathrm{D}t} f_{\alpha}^{ws} \quad \textit{for } \alpha \in \{w, s\} \, . \tag{9.56}$$

SEI Approximation 9.6 is a product breaking approximation that is exact for the case in which the two factors of the product that are split are not correlated with each other. In applying this approximation to the terms in Eq. (9.43), it is useful to recall that on the *ws* interface, $\mathbf{n}_s = -\mathbf{n}_w$. Thus evaluation of the expression in line 16 gives

$$\left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) p_w \right\rangle_{\Omega_{ws},\Omega} = -\frac{\mathrm{D}^{\bar{s}} \varepsilon^{\bar{\bar{s}}}}{\mathrm{D}t} p_w^{ws} \, . \tag{9.57}$$

Line 19 is evaluated with $\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s$ identified as the scalar within the averaging operator so that

$$\left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega} = \frac{\mathrm{D}^{\bar{s}} \varepsilon^{\bar{\bar{s}}}}{\mathrm{D}t} \left(\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s\right)_s^{ws} \, . \tag{9.58}$$

Lines 27 and 28 are handled together. We make use of identity Eq. (2.60), which is expressed for the *ws* interface as $\nabla' \cdot \mathbf{l}'_{ws} = -(\nabla' \cdot \mathbf{n}_s)\mathbf{n}_s$, to obtain

$$\begin{aligned} &\left\langle \left[p_w \mathbf{n}_w - \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s + \gamma_{ws} \left(\nabla' \cdot \mathbf{l}'_{ws}\right) + \rho_{ws} \mathbf{g}_{ws} \cdot \left(\mathbf{l} - \mathbf{l}'_{ws}\right) \right] \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) \right\rangle_{\Omega_{ws},\Omega} \\ &= \left\langle \left[-p_w - \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s - \gamma_{ws} \left(\nabla' \cdot \mathbf{n}_s\right) + \rho_{ws} \mathbf{g}_{ws} \cdot \mathbf{n}_s \right] \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) \right\rangle_{\Omega_{ws},\Omega} . \end{aligned} \tag{9.59}$$

The quantity in brackets on the right side of this equation is zero at equilibrium according to Eqs. (4.52) and (4.53). Then, application of SEI approximation 9.6 yields

$$\begin{aligned} &\left\langle \left[p_w \mathbf{n}_w - \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s + \gamma_{ws} \left(\nabla' \cdot \mathbf{l}'_{ws}\right) + \rho_{ws} \mathbf{g}_{ws} \cdot \left(\mathbf{l} - \mathbf{l}'_{ws}\right) \right] \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) \right\rangle_{\Omega_{ws},\Omega} \\ &= -\left\{ p_w^{ws} + \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega_{ws}} + \left\langle \gamma_{ws} \left(\nabla' \cdot \mathbf{n}_s\right) \right\rangle_{\Omega_{ws},\Omega_{ws}} - \left(\rho_{ws} \mathbf{g}_{ws} \cdot \mathbf{n}_s\right)^{ws} \right\} \frac{\mathrm{D}^{\bar{s}} \varepsilon^{\bar{\bar{s}}}}{\mathrm{D}t} \, . \end{aligned} \tag{9.60}$$

The right side of this equation is a force-flux form where both factors are zero at equilibrium.

It is necessary to introduce another SEI approximation to break the product $\gamma_{ws}\left(\nabla'\cdot\mathbf{n}_s\right)$ so that it can be evaluated. This sort of product will be especially important in considering the multi-fluid flow case where terms involving the curvature of the interface between fluids arises. We state this SEI approximation as follows:

SEI Approximation 9.7 (Product of Curvature and Tension)
The average over the ws interface of a term involving the product of the microscale curvature $\nabla'\cdot\mathbf{n}_s$ with the microscale interfacial tension γ_{ws} can be approximated as the product of the macroscale averages of the two factors such that

$$\left\langle\gamma_{ws}\left(\nabla'\cdot\mathbf{n}_s\right)\right\rangle_{\Omega_{ws},\Omega_{ws}} = \left\langle\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega_{ws}}\left\langle\nabla'\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega_{ws}} = \gamma^{ws}J_s^{ws}\,, \tag{9.61}$$

where $J_s^{ws} = \left\langle\nabla'\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega_{ws}}$ is the average curvature of the ws interface.

Equation (9.60), subject to the additional simplification of Eq. (9.61), is used to modify lines 27 and 28 in Eq. (9.43).

9.5.4 General SEI

When SEI Approximations 9.1 through 9.4 are used to eliminate terms from CEI Eq. (9.43), and SEI approximations 9.5 through 9.7 are employed to introduce mathematical simplifications into this equation, the resulting general form of the SEI is

$$\begin{aligned}
&\frac{1}{\theta^{\overline{\overline{w}}}}\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}}+\varepsilon^{\overline{\overline{w}}}p^{w}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{w}}}+\frac{1}{\theta^{\overline{\overline{s}}}}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}}\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}}-\varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\left(\mathbf{I}-\mathbf{G}^{ws}\right)\right]:\mathbf{d}^{\overline{\overline{ws}}}-\sum_{\alpha\in\mathfrak{I}}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}\right)\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)\\
&+\overset{w\to ws}{M}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{w}}+K_E^{\overline{\overline{w}}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\right]\\
&+\overset{s\to ws}{M}\left[\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{s}}+K_E^{\overline{\overline{s}}}+\psi^{\overline{s}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\overline{\mathbf{C}}^{s}}{3j^{s}}\right)-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\right]\\
&-\left\{\overset{w\to ws}{Q}+\overset{w\to ws}{G}+\left(\overline{E}_w^{\overline{ws}}+K_{Ew}^{\overline{\overline{ws}}}+\psi_w^{\overline{ws}}\right)\overset{w\to ws}{M}\right.\\
&\qquad+\left[\overset{w\to ws}{\mathbf{T}}+\left(\frac{\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}}{2}\right)\overset{w\to ws}{M}\right]\cdot\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\\
&\qquad\left.+p_w^{ws}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\right\}\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)
\end{aligned}$$

$$
\begin{aligned}
&-\Bigg\{\overset{s\to ws}{Q}+\overset{s\to ws}{G}+\left(\overline{E}_s^{\overline{ws}}+K_{Es}^{\overline{\overline{ws}}}+\psi_s^{\overline{ws}}\right)\overset{s\to ws}{M}\\
&\qquad+\left[\overset{s\to ws}{\mathbf{T}}+\left(\frac{\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}}{2}\right)\overset{s\to ws}{M}\right]\cdot\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\\
&\qquad+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\Bigg\}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\\
&-\frac{1}{\theta^{\overline{\overline{w}}}}\Bigg\{\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}}-\nabla\left(\varepsilon^{\overline{\overline{w}}}p^{w}\right)+\varepsilon^{\overline{\overline{w}}}\rho^{w}\nabla\left(\mu^{\overline{w}}+K_E^{\overline{\overline{w}}}+\psi^{\overline{w}}\right)+\varepsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{g}^{\overline{w}}\\
&\qquad-\left[\overset{w\to ws}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{w\to ws}{M}+\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\overset{w\to ws}{M}\right]\Bigg\}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)\\
&-\frac{1}{\theta^{\overline{\overline{ws}}}}\Bigg\{\eta^{\overline{\overline{ws}}}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\cdot\nabla\theta^{\overline{\overline{ws}}}+\nabla\cdot\left[\left(\mathsf{I}-\mathsf{G}^{ws}\right)\varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\right]\\
&\qquad+\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\cdot\nabla\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\\
&\qquad+\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}+\left[\overset{w\to ws}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{w\to ws}{M}+\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\overset{w\to ws}{M}\right]\\
&\qquad+\left[\overset{s\to ws}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{s\to ws}{M}+\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\overset{s\to ws}{M}\right]\Bigg\}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\\
&-\frac{1}{\theta^{\overline{\overline{ws}}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\left[p_w^{ws}+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}+\gamma^{ws}J_s^{ws}-\left(\rho_{ws}\mathbf{g}_{ws}\cdot\mathbf{n}_s\right)_s^{ws}\right]\\
&=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. \qquad (9.62)
\end{aligned}
$$

This general SEI has been derived from the CEI based on the stated set of SEI approximations. At this point, no secondary restrictions have been applied. This means that the same scope of systems described with the original CEI are also describable using the SEI given by Eq. (9.62). Secondary restrictions could be applied to restrict physical processes considered, such as heat transfer, solid compressibility, or interphase transfer of mass. Any combination of these types of restrictions will further simplify this SEI, narrow the scope of problems that can be modeled, and lead to an easier formulation of closure. As an illustration, we will consider closure of one simplified case.

9.6 Example Restricted Application

The objective of this section is to reduce the scope of problems that can be addressed by Eq. (9.62) in anticipation of the development of a closed set of equations. The reduction in scope is accomplished by stating a secondary restriction that limits the processes being studied and allowable properties of the entities. The effect of this restriction is that it will eliminate both terms in the SEI and also some of the terms that appear in the conservation equations. Once these restrictions have been stated, attention will turn to assuring that we have enough conditions and equations to allow the formulation of a closed model that is consistent with the reduced form of the SEI.

9.6.1 Statement of Secondary Restriction

It is important to understand that a secondary restriction is a statement that limits the physical processes one wishes to investigate. The effects of such restrictions are to cause terms in the SEI and conservation equations to drop out, thereby simplifying the problem formulation and narrowing the scope of problems that can be modeled. Here, we will look at a system restricted as follows:

Secondary Restriction 9.1 (Isothermal, No Mass Exchange)
The macroscale single-fluid-phase system of concern is such that:

- *temperatures of all entities are equal and constant such that* $\theta^{\overline{\overline{\alpha}}} = \theta^{\cdot}$ *for* $\alpha \in \mathfrak{I}$ *and all derivatives of temperature are zero;*
- *mass exchange between entities does not occur so that* $\overset{w\to ws}{M} = \overset{s\to ws}{M} = 0$*;*
- *the flow is slow so the deviation kinetic energy term* $K_E^{\overline{\overline{\alpha}}}$ *is of second order smallness for* $\alpha \in \mathfrak{I}$ *and can be neglected; and*
- *the interface density,* ρ^{ws}*, is negligible.*

The conditions on the temperature difference and temperature gradient, which are forces in the EI, along with the condition on the mass exchange flux imply that the values of their conjugate fluxes and forces do not contribute to entropy generation.

With Secondary Restriction 9.1 applied, Eq. (9.62) reduces dramatically to

$$\begin{aligned}
&\frac{1}{\theta^{\cdot}}\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{w}}}p^{w}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{w}}} + \frac{1}{\theta^{\cdot}}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}} \\
&+ \frac{1}{\theta^{\cdot}}\left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}} - \varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\left(\mathbf{I} - \mathbf{G}^{ws}\right)\right]:\mathbf{d}^{\overline{\overline{ws}}} \\
&+ \frac{1}{\theta^{\cdot}}\left[\nabla\left(\varepsilon^{\overline{\overline{w}}}p^{w}\right) - \varepsilon^{\overline{\overline{w}}}\rho^{w}\nabla\left(\mu^{\overline{w}} + \psi^{\overline{w}}\right) - \varepsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{g}^{\overline{w}} + \overset{w\to ws}{\mathbf{T}}\right]\cdot\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) \\
&- \frac{1}{\theta^{\cdot}}\left\{\nabla\cdot\left[\left(\mathbf{I} - \mathbf{G}^{ws}\right)\varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\right] + \overset{w\to ws}{\mathbf{T}} + \overset{s\to ws}{\mathbf{T}}\right\}\cdot\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \\
&- \frac{1}{\theta^{\cdot}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\left[p_{w}^{ws} + \langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\rangle_{\Omega_{ws},\Omega_{ws}} + \gamma^{ws}J_{s}^{ws}\right] = \sum_{\alpha\in\mathfrak{I}}\Lambda^{\overline{\overline{\alpha}}} \geq 0\,. \qquad (9.63)
\end{aligned}$$

Because of the restrictions on temperature and mass exchange, this SEI does not have the ability to model heat transfer or inter-entity mass exchange. The information that can be obtained from a restricted SEI is a subset of the information available from a more general form. An important element of utilizing any SEI is ensuring that sufficient conditions may be extracted to produce a closed equation set. This can be determined by counting the number of unknown variables and the number of equations available to solve the problem.

9.6.2 Count of Variables

For the case of single-fluid-phase flow in a porous medium, there are three entities that are being modeled with $\mathcal{J} = \{w, s, ws\}$. The conservation equations are given in Table 6.3. The full conservation equation set consists of contributions for each of the three entities, $\alpha \in \{w, s, ws\}$. Thus, we have three mass conservation equations ($\mathcal{M}_*^{\overline{\overline{\alpha}}}$), nine components of the three momentum equations ($\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$), three energy equations ($\mathcal{E}_*^{\overline{\overline{\alpha}}}$), three body force potential equations ($\mathcal{G}_*^{\overline{\overline{\alpha}}}$), and the SEI given by Eq. (9.63), for a total of 19 equations. However, as a consequence of Secondary Restriction 9.1, no variables appear in Eq. (9.63) that are introduced into the system description in the energy equation or the body force potential equation (i.e., $E^{\overline{\overline{\alpha}}}$, h^{α}, $h^{\overline{\overline{\alpha}}}$, $K_E^{\overline{\overline{\alpha}}}$, $\overline{E}^{\overline{\overline{\alpha,\kappa}}}$, $K_E^{\overline{\overline{\alpha,\kappa}}}$, $\overset{\kappa\to\alpha}{Q}$, $\mathbf{q}^{\overline{\overline{\alpha}}}$, $\Psi^{\overline{\overline{\alpha}}}$, $\psi^{\overline{\overline{\alpha,\kappa}}}$, $\overset{\kappa\to\alpha}{G}$, $\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}$). Therefore, these latter two equation types are not used for the full system description, reducing the number of equations from 19 to 13. Furthermore, since ρ^{ws} and inter-entity mass exchange are also set to zero in Secondary Restriction 9.1, all the terms in the interface mass balance equation are zero. Therefore, $\mathcal{M}_*^{\overline{\overline{ws}}} = 0$ provides no information; this reduces the available equation count to 12 ($\mathcal{M}_*^{\overline{\overline{\kappa}}}$ for $\kappa \in \{w, s\}$, vector equations $\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$ for $\alpha \in \{w, s, ws\}$, and Eq. (9.63)).

The variables that appear in the equation set for modeling the system are members of the set $\mathcal{V}$ where

$$\begin{aligned}\mathcal{V} = \{&\varepsilon^{\overline{\overline{\alpha}}}, \rho^{\kappa}, \mathbf{v}^{\overline{\alpha}}, \mathbf{g}^{\overline{\kappa}}, \overset{ws\to\kappa}{\mathbf{T}}, \mathbf{t}^{\overline{\overline{\alpha}}}, p^{w}, p_{w}^{ws}, \mathbf{t}^{s}, \gamma^{ws}, \mathbf{G}^{ws}, \\ &\mu^{\overline{w}}, \psi^{\overline{w}}, \langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ws}, \Omega_{ws}}, J_s^{ws}, \Lambda^{\overline{\overline{\alpha}}}\} \quad \text{for } \kappa \in \mathcal{J}_{\mathrm{P}}, \alpha \in \mathcal{J}\,.\end{aligned} \tag{9.64}$$

Thus with vectors contributing three variables and tensors nine, $\mathcal{V}$ contains 81 members. In light of the fact that we have identified 12 equations, a deficit of 69 equations or conditions remains for the system to be closed. This deficit reduces immediately to 54 by recognizing that each tensor is symmetric and thus consists of only six independent members rather than nine. Nevertheless, even for this relatively simple physical problem, the formulation of needed additional conditions is not trivial. Fortunately, the SEI provides helpful guidance that can be used to supplement the equation set. The requirement that these additional conditions must be specified explicitly is a strength of the TCAT approach as the assumptions made can be revisited to improve a model.

9.6.3 *Reduction in Number of Variables*

If we take into account the symmetry of the stress tensor, Eq. (9.63) has 25 pairs of forces and fluxes on the left side that can be used to suggest closure relations. This still leaves a deficit of 29 conditions that are needed to obtain full closure. In this subsection, we will identify conditions and assumptions employed to eliminate this deficit of equations needed to produce a solvable system.

Gravity (6)

The microscale gravity is assumed to be a known constant vector. Thus, its average will be equal to the same constant. Specification of the vectors $\mathbf{g}^{\overline{w}}$ and $\mathbf{g}^{\overline{s}}$ reduces the number of variables by six leaving 23.

Gravitational Potential of the *w* phase (1)

At the microscale, we know that $\nabla\psi_w + \mathbf{g}_w = 0$. When the distribution of the space within an REV occupied by the w phase is uniform, the macroscale gravitational potential satisfies the condition $\nabla\psi^{\overline{w}} + \mathbf{g}^{\overline{w}} = 0$. When the distribution of the w phase in the system is not uniform, $\psi^{\overline{w}}$ will not be a linear function of macroscale elevation. We will consider that $\nabla\psi^{\overline{w}}$ can be specified in Eq. (9.63) and the number of unknowns is reduced by one.

Entropy Production (2)

The entropy production rates, $\Lambda^{\overline{\overline{w}}}$, $\Lambda^{\overline{\overline{s}}}$, and $\Lambda^{\overline{\overline{ws}}}$, appear in the formulation only in Eq. (9.63) and only as a sum rather than individually. Thus rather than considering the values of the three individual production rates as unknowns, we will concern ourselves only with their sum. This observation decreases the number of unknowns by two.

Volume Fraction Condition (1)

The system is comprised of two phases that occupy volume. Thus the fractions of space occupied by the two phases must sum to 1, with

$$\varepsilon^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{s}}} = 1 \,. \tag{9.65}$$

By this equation, knowledge of $\varepsilon^{\overline{\overline{w}}}$ determines $\varepsilon^{\overline{\overline{s}}}$ and thus eliminates one unknown variable.

Specification of p_w^{ws} (1)

The pressure in the w phase appears averaged over the boundary of the w phase and over the w phase itself. In many cases, the difference between these averages will be negligible. However, rather than imposing this constraint at this time, we will assume that p_w^{ws} can be specified as a function of p^w and the pressure-like quantity that is a product of interfacial tension and curvature, $\gamma^{ws}J_s^{ws}$, such that

$$p_w^{ws} = p_w^{ws}\left(p^w, \gamma^{ws}J_s^{ws}\right) . \tag{9.66}$$

This approximation reduces the number of unknown variables by one. However the burden of having to determine the form of this function is introduced.

Morphology (7)

The orientation tensor, G^{ws}, is an important quantity that accounts at the macroscale for any orientation preferences of the solid material. Here, for simplicity, we will assume that the orientation of the grains is random, so that

$$\mathsf{G}^{ws} = \mathsf{I}/3 . \tag{9.67}$$

This assumption can be changed for materials that exhibit directional dependence. The average curvature of the grains, J_s^{ws}, is considered to be known. Specification of G^{ws} and J_s^{ws} reduces the number of unknown variables by seven.

Equations of State (4)

We will assume that equations of state in terms of macroscale variables can be postulated similarly to state equations for microscale variables. Thus, with temperature and chemical composition considered constant, we propose

$$\rho^w = \rho^w(p^w) , \tag{9.68}$$

$$\rho^s = \rho^s(\langle \mathbf{n}_s\cdot\mathbf{t}_s\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}) , \tag{9.69}$$

$$\mu^{\overline{w}} = \mu^{\overline{w}}(p^w) , \tag{9.70}$$

and

$$\gamma^{ws} = \text{constant} . \tag{9.71}$$

If desired, γ^{ws} can be postulated to be a function of the pressure at the interface. However, for our purposes, a constant interfacial tension suffices. This set of state equations will require parameterization, but reduces the excess number of variables by four.

Interface Evolution (1)

An approximate interface evolution equation was derived in Chap. 8 and is given as Eq. (8.20), repeated here for convenience, with

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{ws}}}}{\mathrm{D}t} - J_s^{ws}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} + \varepsilon^{\overline{\overline{ws}}}\mathbf{G}^{ws}{:}\mathbf{d}^{\overline{\overline{s}}} = 0\,. \tag{9.72}$$

This relation reduces the equation deficit by one.

Solid-phase Stress Tensor (6)

Appearing in the list of variables is the average of the microscale solid-phase stress, $\mathbf{t}^s$. The general form of the microscale solid stress based on kinematic considerations is given in Eq. (4.25), and therefore its average can be calculated with

$$\mathbf{t}^s = \left\langle \frac{2}{j_s}\left(\nabla_X \mathbf{x}_s\right)^{\mathrm{T}} \cdot \boldsymbol{\sigma}_s \cdot \nabla_X \mathbf{x}_s \right\rangle_{\Omega_s,\Omega_s} . \tag{9.73}$$

There is a need to approximate the average of the product of terms that appears on the right side. This will be done later, along with restrictions that limit the behavior of the solid material. For now, we merely state that we will specify $\mathbf{t}^s$ and thereby impose six restrictions.

The preceding identification of 29 variables and equations still leaves a deficit of 25 equations to close the system. The identification of these 25 additional conditions is guided by the force-flux pairs that appear in the SEI, Eq. (9.63).

9.6.4 Conjugate Force-flux Closure

As was the case with the closure of microscale models in Chap. 5, the closure procedure that makes use of the EI can be formulated in two alternative ways. First, a force-flux closure can be posed whereby a flux is considered to be linearly related only to its conjugate force. A second, more general, approach allows each flux to be proportional to all the forces. In either event, the formulation of closure relations is approximate and provides non-unique expressions that are subject to scrutiny in regard to how well they describe a system of interest. These closure expressions are built on SEI approximations as well as the approximations of variables. Thus, by altering any of the employed assumptions, a considerable range in the hierarchy of closed models can be obtained. Although the need to impose a large set of approximations to arrive at a model may at first seem unattractive, the fact that all assumptions that underpin a model are explicitly known provides a clear path for research to improve a model. This is superior to a less specific route to a closed model of unknown rigor. The last steps of the closure process will be illustrated here to provide an instance of a closed model from within the hierarchy. We will list the conjugate force-flux closure relations that result from Eq. (9.63) in the order of the forces that appear in this equation.

Forces: $\mathbf{d}^{\overline{\overline{w}}}$, $\mathbf{d}^{\overline{\overline{s}}}$, and $\mathbf{d}^{\overline{\overline{ws}}}$ (18)

The multipliers of the rates of strain tensors are considered to have zero-order dependence on the rate of strain. This implies that the macroscale gradients of velocity do not contribute to the stress tensor. Such an approximation is reasonable for a porous medium wherein the microscale gradients in the pore space may be significant, but gradients of average velocity will be small. With this approximation, the fluxes that multiply the forces $\mathsf{d}^{\overline{\overline{\alpha}}}$ are zero such that

$$\mathsf{t}^{\overline{\overline{w}}} = -p^w\mathsf{I}\,, \tag{9.74}$$

$$\mathsf{t}^{\overline{\overline{s}}} = \mathsf{t}^s\,, \tag{9.75}$$

and

$$\mathsf{t}^{\overline{\overline{ws}}} = \gamma^{ws}\left(\mathsf{I} - \mathsf{G}^{ws}\right)\,. \tag{9.76}$$

These equations provide 18 closure conditions.

Forces: $\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right)$ and $\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right)$ (6)

We consider the fluxes to be linearly related to each of the conjugate relative velocity forces.[3] We know that both of these forces are zero at equilibrium, and that away from equilibrium the flow process produces entropy. The resulting linearized expressions are

$$\nabla\left(\varepsilon^{\overline{\overline{w}}}p^w\right) - \varepsilon^{\overline{\overline{w}}}\rho^w\nabla\left(\mu^{\overline{w}} + \psi^{\overline{w}}\right) - \varepsilon^{\overline{\overline{w}}}\rho^w\mathbf{g}^{\overline{w}} + \overset{w\to ws}{\mathbf{T}} = \hat{\mathsf{R}}^w\cdot\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) \tag{9.77}$$

and

$$-\nabla\cdot\left[\left(\mathsf{I} - \mathsf{G}^{ws}\right)\varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\right] - \overset{w\to ws}{\mathbf{T}} - \overset{s\to ws}{\mathbf{T}} = \hat{\mathsf{R}}^{ws}\cdot\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right)\,. \tag{9.78}$$

These vector equations provide six closure conditions. However, the tensors $\hat{\mathsf{R}}^w$ and $\hat{\mathsf{R}}^{ws}$ that have been introduced will have to be estimated or specified in terms of problem variables. The signs on these tensor coefficients are chosen for each term so that the tensors are positive semi-definite.

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[3] A more general closure scenario would allow each flux to be linearly related to both of the relative velocity forces. Inherent in conjugate force-flux closure is the approximation that cross-coupling is not important.

Force: $\boldsymbol{p_w^{ws}} + \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}} + \boldsymbol{\gamma^{ws}J_s^{ws}}$ (1)

This force does not appear as one of the original forces identified for the CEI in Table 9.1, although we know it is zero at equilibrium based on Eq. (7.115). It is introduced into the problem by SEI Approximation 9.6. The requirements that the conjugate flux and force will both be zero at equilibrium and the stipulation that this process be entropy-producing suggest the linear relation

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} = -\hat{c}\left(p_w^{ws} + \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}} + \gamma^{ws}J_s^{ws}\right) . \tag{9.79}$$

Note that the approximation given in Eq. (9.66) may be used to replace p_w^{ws} with some combination of p^w and $\gamma^{ws}J_s^{ws}$.

9.6.5 Closed Conservation Equation Set

The equations and approximations in Sect. 9.6.3 and the closure conditions in Sect. 9.6.4 are sufficient to obtain a closed set of conservation equations. We will provide the set here with the approximations inserted into the mass and momentum conservation equations listed in Table 6.3.

Mass Conservation for *w* and *s* Phases

With no mass exchange and $\rho^{ws} = 0$, the only mass conservation equations are those for the w and s phases. These equations are

$$\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{P}} . \tag{9.80}$$

Momentum Conservation for the *w* Phase

The momentum conservation equation for the fluid phase makes use of the closure relations for the stress tensor given in Eq. (9.74) and the closure relation stated in Eq. (9.77). For the w phase, the momentum equation is

$$\frac{\mathrm{D}^{\overline{w}}(\varepsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{v}^{\overline{w}})}{\mathrm{D}t} + \varepsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{v}^{\overline{w}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{w}}}\rho^{w}\nabla\left(\mu^{\overline{w}} + \psi^{\overline{w}}\right) + \hat{\mathsf{R}}^{w}\cdot\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) = \mathbf{0} . \tag{9.81}$$

Momentum Conservation for the *ws* Interface

For the massless *ws* interface, the momentum equation in conjunction with Eq. (9.78) provides the trivial condition

$$\hat{\mathsf{R}}^{ws}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)=\mathbf{0}\,. \tag{9.82}$$

Momentum Conservation for the *s* Phase

The solid-phase momentum equation makes use of the relation for the stress tensor given by Eq. (9.75), closure relations Eqs. (9.77) and (9.78), and the momentum equation for the interface, Eq. (9.82). Combination of these equations with the momentum equation $\mathcal{P}_{*}^{\overline{\overline{s}}}$ provides

$$\begin{aligned}\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{s}}}\rho^{s}\mathbf{v}^{\overline{s}})}{\mathrm{D}t}&+\varepsilon^{\overline{\overline{s}}}\rho^{s}\mathbf{v}^{\overline{s}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\rho^{s}\mathbf{g}^{\overline{s}}-\varepsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{g}^{\overline{w}}-\varepsilon^{\overline{\overline{w}}}\rho^{w}\nabla\left(\mu^{\overline{w}}+\psi^{\overline{w}}\right)\\&-\nabla\cdot\left[\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}-\varepsilon^{\overline{\overline{w}}}p^{w}\mathsf{I}+\left(\mathsf{I}-\mathsf{G}^{ws}\right)\varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\right]=\hat{\mathsf{R}}^{w}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)\,.\end{aligned} \tag{9.83}$$

Entropy Generation Rate for the System

The system entropy generation rate is obtained from Eq. (9.63) by replacing the fluxes with their linear representations in terms of forces as given by Eqs. (9.77)–(9.79) and invoking the conditions of Eqs. (9.74)–(9.76). The result is

$$\begin{aligned}\frac{1}{\theta}\Big[&\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)\cdot\hat{\mathsf{R}}^{w}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)\\&+\hat{c}\left(p_{w}^{ws}+\langle\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\rangle_{\Omega_{ws},\Omega_{ws}}+\gamma^{ws}J_{s}^{ws}\right)^{2}\Big]=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,.\end{aligned} \tag{9.84}$$

The requirement that the entropy generation rate be non-negative is guaranteed when $\hat{\mathsf{R}}^{w}$ is positive semi-definite and $\hat{c}$ is non-negative .

9.7 Model of Fluid and Elastic Solid

Here we follow a derivation applied for two-fluid-phase flow [3], which is readily adapted to the single-fluid-phase flow case. The equations developed in the last subsection provide a complete and closed model of single-phase flow in a porous medium. It is crucial to understand that this closed set is achieved only with the stipulations of the variables as described in Sect. 9.6.3. In that subsection, variables that require functional forms or specification were identified. Here, we will introduce some simplifications and explicit relations that lead to appropriate, and further restricted, models. Determination of the form of the solid stress, $\mathbf{t}^{\overline{\overline{s}}} = \mathbf{t}^s$, provides an interesting challenge. An example of this determination will be presented next before proceeding with additional simplification of the model equations.

9.7.1 Compressible Elastic Solid with Small Deformation

Equation (9.73), in conjunction with Eq. (9.75), provides an expression for the solid-phase stress tensor. We can also write the solid-phase stress tensor as

$$\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}} = -\varepsilon^{\overline{\overline{s}}} p^s \mathsf{I} + \varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}} . \tag{9.85}$$

where, as yet, neither p^s nor $\boldsymbol{\tau}^{\overline{\overline{s}}}$ has been specified.

The group of terms in brackets in Eq. (9.83) is identified as the total stress, t_T, which is a weighted sum of the stress tensors of the s, w, and ws entities, where the weighting factors are the entity densities, such that

$$\mathsf{t}_T = \varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}} , \tag{9.86}$$

or

$$\mathsf{t}_T = -p_T \mathsf{I} + \varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}} , \tag{9.87}$$

where

$$p_T = \varepsilon^{\overline{\overline{s}}} p^s + \varepsilon^{\overline{\overline{w}}} p^w - \frac{2}{3}\varepsilon^{\overline{\overline{ws}}}\gamma^{ws} . \tag{9.88}$$

In writing this expression, we have made use of the approximation given in Eq. (9.67). The trace of t_T can be determined as

$$\frac{\mathsf{t}_T{:}\mathsf{I}}{3} = \frac{\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}}{:}\mathsf{I}}{3} + \frac{\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}}{:}\mathsf{I}}{3} + \frac{\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}}{:}\mathsf{I}}{3} . \tag{9.89}$$

Based on Eq. (9.87), this may alternatively be written

$$\frac{\mathsf{t}_T{:}\mathsf{I}}{3} = -p_T + \frac{\varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}}{:}\mathsf{I}}{3} . \tag{9.90}$$

We normalize the trace of the total stress with the average of the normal component of the stress on the solid surface so that Eq. (9.90) becomes

$$\frac{\mathsf{t}_T{:}\mathsf{I}}{3\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}} = -\frac{p_T}{\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}} + \frac{\varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}}{:}\mathsf{I}}{3\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}} . \tag{9.91}$$

The ratio on the left side of this equation is equal to 1 as it is composed of alternative expressions for the total stress that will act on the solid. The leading term on the right is the Biot coefficient [2], $\hat{\alpha}_B$, such that

$$\hat{\alpha}_B = -\frac{p_T}{\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}} \ . \tag{9.92}$$

Thus Eq. (9.91) may be rewritten

$$1 = \hat{\alpha}_B + \frac{\varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}}{:}\mathsf{I}}{3\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}} \ . \tag{9.93}$$

We now follow arguments analogous to those used in the derivation from Eqs. (5.56)–(5.61) for the microscale viscous stress tensor in an isotropic medium. Here, for the solid, we assume that the deformations are small so that effective stress, $\varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}}$, is a function of e^s, the macroscale infinitesimal strain tensor. If the solid is assumed to be linear, elastic, and isotropic, and if all deformations are small, then the effective stress tensor is

$$\varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}} = \frac{\hat{E}}{1+\hat{\nu}}\mathsf{e}^s + \frac{\hat{\nu}\hat{E}}{(1-2\hat{\nu})(1+\hat{\nu})}\mathsf{e}^s{:}\mathsf{II} \, . \tag{9.94}$$

where $\hat{E}$ is Young's modulus, $\hat{\nu}$ is Poisson's ratio, and e^s is the infinitesimal strain tensor.[4] The tensor e^s is the infinitesimal form of $\mathsf{E}^s = (\mathsf{C}^s - \mathsf{I})/2$ defined by

$$\mathsf{e}^s = \frac{1}{2}\left[\nabla\mathbf{u}^{\overline{s}} + \left(\nabla\mathbf{u}^{\overline{s}}\right)^{\mathrm{T}}\right] \ , \tag{9.95}$$

where $\mathbf{u}^{\overline{s}}$ is the displacement vector. In contrast to fluids, the solid stress tensor is related to the amount of deformation rather than to the rate of deformation because a solid at equilibrium can support a shear stress. The rate of displacement is the velocity.

One third of the trace of the effective stress tensor in Eq. (9.94) is then

$$\frac{\varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}}{:}\mathsf{I}}{3} = \frac{\hat{E}}{3(1-2\hat{\nu})}\mathsf{e}^s{:}\mathsf{I} = \hat{K}_T\mathsf{e}^s{:}\mathsf{I} \, , \tag{9.96}$$

where $\hat{K}_T$ is the bulk modulus of the skeleton, defined to be related to Young's modulus and the Poisson ratio by

$$\hat{K}_T = \frac{\hat{E}}{3(1-2\hat{\nu})} \ . \tag{9.97}$$

Substitution of Eq. (9.96) into Eq. (9.93) yields

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[4] The use of the word "infinitesimal" refers to the amount of deformation, not the scale of the deformation. Additionally, note that Eq. (9.94) consists of two coefficients, as in Eq. (5.61), although the identification of the coefficients is different. Alternatively, Eq. (9.94) can be written in a form similar to Eq. (5.59) as $\varepsilon^{\overline{\overline{s}}}\boldsymbol{\tau}^{\overline{\overline{s}}} = 2\hat{\mu}\mathsf{e}^s + \hat{\lambda}\mathsf{e}^s{:}\mathsf{II}$ where the two coefficients $\hat{\mu}$ and $\hat{\lambda}$ are called Lamé constants.

$$\hat{\alpha}_B = 1 - \frac{\hat{K}_T \mathbf{e}^s{:}\mathbf{I}}{\langle \mathbf{n}_s{\cdot}\mathbf{t}_s{\cdot}\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}}} \,. \tag{9.98}$$

The averaged bulk modulus of the solid grains, $\hat{K}_S$, as opposed to that for the skeleton, relates the decrease in volume of the solid material to the average normal force on the solid surface [5], as given by

$$\frac{1}{\hat{K}_S} = \frac{\mathbf{e}^s{:}\mathbf{I}}{\langle \mathbf{n}_s{\cdot}\mathbf{t}_s{\cdot}\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}}} \,. \tag{9.99}$$

Thus the last two equations show that the Biot coefficient for a compressible solid may be expressed as

$$\hat{\alpha}_B = 1 - \frac{\hat{K}_T}{\hat{K}_S} \,. \tag{9.100}$$

When the solid material, as opposed to the bulk solid structure including pore space, has very little compressibility, $1/\hat{K}_S$ is small enough that the Biot coefficient is approximately 1.

Use of Eqs. (9.92), (9.94), and (9.100) in Eq. (9.87) gives the total stress as

$$\mathbf{t}_T = \left(1 - \frac{\hat{K}_T}{\hat{K}_S}\right) \langle \mathbf{n}_s{\cdot}\mathbf{t}_s{\cdot}\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}} \mathbf{I} + \frac{\hat{E}}{1+\hat{\nu}} \mathbf{e}^s + \frac{\hat{\nu}\hat{E}}{(1-2\hat{\nu})(1+\hat{\nu})} \mathbf{e}^s{:}\mathbf{I}\mathbf{I} \,. \tag{9.101}$$

When p_w^{ws} is approximately equal to p^w and the terms involving surface tension are negligible, this equation simplifies to the form typically found in the literature (e.g., as in [1, 2]),

$$\mathbf{t}_T = -\left(1 - \frac{\hat{K}_T}{\hat{K}_S}\right) p^w \mathbf{I} + \frac{\hat{E}}{1+\hat{\nu}} \mathbf{e}^s + \frac{\hat{\nu}\hat{E}}{(1-2\hat{\nu})(1+\hat{\nu})} \mathbf{e}^s{:}\mathbf{I}\mathbf{I} \,. \tag{9.102}$$

Usually, flows and deformations in porous media are slow such that the inertial terms in the momentum equations are negligible. In such cases, mass conservation is described by Eq. (9.80), but the first two terms in Eq. (9.81) are neglected so that the fluid momentum equation becomes

$$\varepsilon^{\overline{\overline{w}}} \rho^w \nabla \left(\mu^{\overline{w}} + \psi^{\overline{w}}\right) + \hat{\mathbf{R}}^w \cdot \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) = \mathbf{0} \,. \tag{9.103}$$

With the inertial terms neglected and Eqs. (9.103) and (9.86) employed, the solid-phase[5] momentum equation, Eq. (9.83), reduces to

$$\varepsilon^{\overline{\overline{s}}} \rho^s \mathbf{g}^{\overline{s}} + \varepsilon^{\overline{\overline{w}}} \rho^w \mathbf{g}^{\overline{w}} + \nabla{\cdot}\mathbf{t}_T = \mathbf{0} \,, \tag{9.104}$$

---

[5] From another perspective, Eq. (9.83) is the momentum equation for the system as a whole. In any event, it is an independent expression of momentum conservation that can be used in conjunction with the w phase momentum equation to describe the system behavior.

where Eq. (9.101) or Eq. (9.102) can be used to describe the total stress tensor. Mass conservation for the solid phase as described by Eq. (9.80) completes the simplified closed set of equations that models both the solid and fluid phases.

9.7.2 Passive Solid Phase

A commonly used model when one is interested primarily in the fluid flow treats the solid implicitly as a passive element whose state is determined completely by its response to the fluid phase. In this case, the solid-phase momentum equation, such as Eq. (9.104), is ignored; and the mass conservation expressions for each phase given by Eq. (9.80) are combined to provide a single mass conservation equation for the system. In some cases, the surviving mass and momentum conservation equations can also be combined to give a single equation that describes the system. This model will be developed here for the isothermal case.

For the w phase, mass conservation is described by Eq. (9.80) as

$$\frac{\mathrm{D}^{\overline{w}}(\varepsilon^{\overline{\overline{w}}}\rho^{w})}{\mathrm{D}t} + \varepsilon^{\overline{\overline{w}}}\rho^{w}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{w}}} = 0\,. \tag{9.105}$$

We can apply the identity Eq. (7.49), with α replaced by w, to change the material derivative so that it is with respect to the solid velocity and also note that

$$\mathsf{I}{:}\mathbf{d}^{\overline{\overline{w}}} = \nabla\cdot(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}) + \mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}}\,. \tag{9.106}$$

Thus, Eq. (9.105) may be re-expressed as

$$\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{w}}}\rho^{w})}{\mathrm{D}t} + (\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}})\cdot\nabla(\varepsilon^{\overline{\overline{w}}}\rho^{w}) + \varepsilon^{\overline{\overline{w}}}\rho^{w}\nabla\cdot(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}) + \varepsilon^{\overline{\overline{w}}}\rho^{w}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}} = 0\,, \tag{9.107}$$

or, after application of the product rule to the second and third terms,

$$\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{w}}}\rho^{w})}{\mathrm{D}t} + \nabla\cdot\left[\varepsilon^{\overline{\overline{w}}}\rho^{w}(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}})\right] + \varepsilon^{\overline{\overline{w}}}\rho^{w}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}} = 0\,. \tag{9.108}$$

The solid-phase mass conservation equation based on Eq. (9.80) may be rearranged to

$$\frac{1}{\varepsilon^{\overline{\overline{s}}}\rho^{s}}\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{s}}}\rho^{s})}{\mathrm{D}t} + \mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}} = 0\,. \tag{9.109}$$

Combination of this equation with Eq. (9.108) to eliminate $\mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}}$ yields

$$\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{w}}}\rho^{w})}{\mathrm{D}t} - \frac{\varepsilon^{\overline{\overline{w}}}\rho^{w}}{\varepsilon^{\overline{\overline{s}}}\rho^{s}}\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{s}}}\rho^{s})}{\mathrm{D}t} + \nabla\cdot\left[\varepsilon^{\overline{\overline{w}}}\rho^{w}(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}})\right] = 0\,. \tag{9.110}$$

We next make use of Eq. (9.65) to eliminate $\varepsilon^{\overline{\overline{s}}}$ from this equation in favor of $\varepsilon^{\overline{\overline{w}}}$. After application of the product rule to the time derivatives and further rearrangement, the following expression is obtained,

$$-\frac{\rho^w}{(1-\varepsilon^{\overline{\overline{w}}})\rho^s}\frac{\mathrm{D}^{\overline{s}}[(1-\varepsilon^{\overline{\overline{w}}})\rho^s]}{\mathrm{D}t}+\varepsilon^{\overline{\overline{w}}}\frac{\mathrm{D}^{\overline{s}}\rho^w}{\mathrm{D}t}+\frac{(1-\varepsilon^{\overline{\overline{w}}})\rho^w}{\rho^s}\frac{\mathrm{D}^{\overline{s}}\rho^s}{\mathrm{D}t}$$
$$+\nabla\cdot\left[\varepsilon^{\overline{\overline{w}}}\rho^w(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}})\right]=0\,. \tag{9.111}$$

Because, at present, we are interested in an isothermal system and the solid is being treated as passive, it is common to consider that the mass of solid per total volume, $(1-\varepsilon^{\overline{\overline{w}}})\rho^s$, and the phase densities, ρ^w and ρ^s, are functions only of the macroscale fluid-phase pressure, p^w. Thus we propose state equations for these three terms as

$$\hat{\alpha}_{\mathrm{B}s}=-\frac{1}{(1-\varepsilon^{\overline{\overline{w}}})\rho^s}\frac{\mathrm{d}[(1-\varepsilon^{\overline{\overline{w}}})\rho^s]}{\mathrm{d}p^w}\,, \tag{9.112}$$

$$\hat{\beta}_w=\frac{1}{\rho^w}\frac{\mathrm{d}\rho^w}{\mathrm{d}p^w}\,, \tag{9.113}$$

and

$$\hat{\beta}_s=\frac{1}{\rho^s}\frac{\mathrm{d}\rho^s}{\mathrm{d}p^w}\,, \tag{9.114}$$

where $\hat{\alpha}_{\mathrm{B}s}$ is the bulk compressibility of the solid phase, $\hat{\beta}_w$ is the compressibility of the fluid phase, and $\hat{\beta}_s$ is the compressibility of the solid phase. Substitution of these three state equations into Eq. (9.111) provides

$$\rho^w\left[\hat{\alpha}_{\mathrm{B}s}+\varepsilon^{\overline{\overline{w}}}\hat{\beta}_w+(1-\varepsilon^{\overline{\overline{w}}})\hat{\beta}_s\right]\frac{\mathrm{D}^{\overline{s}}p^w}{\mathrm{D}t}+\nabla\cdot\left[\varepsilon^{\overline{\overline{w}}}\rho^w(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}})\right]=0\,. \tag{9.115}$$

Because the velocity of the solid is very slow and pressure will propagate quickly, it is reasonable to assume that

$$\left|\frac{\partial p^w}{\partial t}\right|\gg\left|\mathbf{v}^{\overline{s}}\cdot\nabla p^w\right|\,. \tag{9.116}$$

Based on this approximation, the material derivative in Eq. (9.115) is replaced by a partial time derivative so that the resultant mass conservation equation is

$$\rho^w\left[\hat{\alpha}_{\mathrm{B}s}+\varepsilon^{\overline{\overline{w}}}\hat{\beta}_w+(1-\varepsilon^{\overline{\overline{w}}})\hat{\beta}_s\right]\frac{\partial p^w}{\partial t}+\nabla\cdot\left[\varepsilon^{\overline{\overline{w}}}\rho^w(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}})\right]=0\,. \tag{9.117}$$

Equation (9.117) is to be solved in conjunction with Eq. (9.103) when the compressibility coefficients have been determined, the resistance tensor $\hat{\mathbf{R}}^w$ is specified, $\mu^{\overline{w}}$ is specified as a function of p^w, and $\psi^{\overline{w}}$ can be specified. The simplest meaningful situation that arises is when the porous matrix is isotropic so that

$$\hat{\mathsf{R}}^{w} = \hat{R}^{w}\mathsf{I}\,. \tag{9.118}$$

Additionally, if the variability of functions is small so that the gradient of deviations between microscopic and macroscopic variables is negligible in comparison to the gradients of macroscale variables, the Gibbs-Duhem equation given in Eq. (7.33) simplifies for an isothermal fluid composed of a single species to the gradient operator form given by

$$-\varepsilon^{\overline{\overline{w}}}\nabla p^{w} + \varepsilon^{\overline{\overline{w}}}\rho^{w}\nabla\mu^{\overline{w}} = \mathbf{0}\,. \tag{9.119}$$

Lastly, when the gradient in volume fraction is small,

$$\nabla\psi^{\overline{w}} + \mathbf{g}^{\overline{w}} = \mathbf{0}\,, \tag{9.120}$$

and $\mathbf{g}^{\overline{w}}$ is the gravitational vector for problems without other external body forces. Substitution of Eqs. (9.118), (9.119), and (9.120) into Eq. (9.103) provides the momentum equation for the fluid,

$$\varepsilon^{\overline{\overline{w}}}\left(\nabla p^{w} - \rho^{w}\mathbf{g}^{\overline{w}}\right) + \hat{R}^{w}\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) = \mathbf{0}\,. \tag{9.121}$$

We define a new coefficient, $\hat{K}^{w}$, according to

$$\hat{K}^{w} = \frac{\varepsilon^{\overline{\overline{w}}2}\rho^{w}}{\hat{R}^{w}} \tag{9.122}$$

so that Eq. (9.121) can be written

$$\hat{K}^{w}\left(\nabla p^{w} - \rho^{w}\mathbf{g}^{\overline{w}}\right) + \varepsilon^{\overline{\overline{w}}}\rho^{w}\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) = \mathbf{0}\,. \tag{9.123}$$

This form of the momentum equation is known as Darcy's law. It may be employed to eliminate the velocity term from Eq. (9.117) to obtain what is commonly called the groundwater flow equation,

$$\rho^{w}\left[\hat{\alpha}_{\mathrm{B}s} + \varepsilon^{\overline{\overline{w}}}\hat{\beta}_{w} + (1-\varepsilon^{\overline{\overline{w}}})\hat{\beta}_{s}\right]\frac{\partial p^{w}}{\partial t} - \nabla\cdot\left[\hat{K}^{w}\left(\nabla p^{w} - \rho^{w}\mathbf{g}^{\overline{w}}\right)\right] = 0\,. \tag{9.124}$$

This equation contains a single unknown variable, p^{w}, and thus by itself describes single-fluid-phase flow in a porous medium. It can be solved after specification of the appropriate boundary conditions for p^{w}. The path to this equation based on all the elements of the TCAT approach is certainly rather tortuous. Although this equation is typically provided based on simpler derivations, by explicitly identifying all the assumptions made, we have a clear picture of the approximations that could undermine efforts to describe a system with this equation. Less restrictive models were encountered on the way to Eq. (9.124) that might be more suitable for some complex problems.

9.8 Summary

In this chapter, we have illustrated the TCAT approach for deriving a macroscale model for single-fluid-phase flow in a porous medium. Based on macroscale entropy, conservation and thermodynamic equations, the CEI of Eq. (9.43) has been derived and is of archival value. SEI approximations were identified in Sects. 9.5.2 and 9.5.3 that facilitated expression of a general SEI in Eq. (9.62) that is a sum of macroscale force-flux products. The use of secondary restrictions was also demonstrated in constraining the system to be isothermal with no interphase mass exchange. The restrictions imposed led to the simplified SEI of Eq. (9.63). The closure procedure for this case was demonstrated and led to mass and momentum conservation equations for a fluid phase and an elastic solid phase. Eqs. (9.80), (9.103), and (9.104). This equation set was further simplified for the situation where the solid phase is modeled only passively such that the system is described by a single equation that is a composite of mass conservation equations for both phases and the momentum conservation equation for the fluid. The result, Eq. (9.124), is one form of the groundwater flow equation.

The CEI and SEI's derived in this chapter provide a basis for derivation of a considerable breadth of single-phase-flow models. Potential models that could be built on these inequalities include nonisothermal systems, interphase transport, moderately compressible flows, plastic deformation, the role of potentials in driving flow, interfaces that accumulate mass, and non-Darcy flow. In addition, microscale imaging and computer simulation methods provide a means to demonstrate and develop a correspondence between the microscale and the macroscale that is embodied within TCAT models.

The approach taken for formulation of a single-phase-flow model in this chapter is illustrative of the general TCAT model formulation procedure depicted in Fig. 9.1 based on macroscale equations. The same steps will be followed in deriving models of other macroscale systems, although the detailed equations within each step will be different. In the next two chapters, species transport and two-fluid-phase flow, respectively, will be considered.

Exercises

9.1. Prove Eq. (9.33),

$$\sum_{\alpha\in\mathfrak{I}}\left(\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\overset{\kappa\rightarrow\alpha}{M}\,\overline{\eta}^{\overline{\overline{\alpha,\kappa}}}+\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\overset{\kappa\rightarrow\alpha}{\Phi}\right)=0\,.$$

9.2. Start with the general SEI given in Eq. (9.62). For the present exercise, make use of the Secondary Restriction

Secondary Restriction 9.2 (No Interface Properties)
The macroscale single-fluid-phase system of concern is such that:

- *Properties of the ws interface are negligible including* ρ^{ws}, $\mathbf{t}^{\overline{\overline{ws}}}$, $E^{\overline{\overline{ws}}}$, $\mathbf{q}^{\overline{\overline{ws}}}$, h^{ws}, $h^{\overline{\overline{ws}}}$, $\eta^{\overline{\overline{ws}}}$, *and* γ^{ws}*; and*
- *the flow is slow so the deviation kinetic energy term* $K_E^{\overline{\overline{\alpha}}}$ *is of second order smallness and can be neglected.*

a. Show that the conservation equations for the interfaces are jump conditions that provide relations for transfer between the *w* and *s* phases.
b. Simplify Eq. (9.62) to a form that takes into account Secondary Restriction 9.2.

9.3. Simplify the SEI of exercise 9.2b for the isothermal case with no interphase mass transfer. Discuss reasons for differences between this result and Eq. (9.63).

9.4. Obtain the closed equation set needed for the situation described in exercise 9.3.

9.5. Simplify the general SEI of exercise 9.2b for the non-isothermal case with no interphase mass transfer (Hint: $\theta^{\overline{\overline{ws}}}$ should not appear in the result.).

9.6. Obtain the closed equation set for the situation described in exercise 9.4.

9.7. As an alternative to conjugate force-flux closure employed in Sect. 9.6.4, cross-coupled closure may be employed as described for a microscale closure problem in Sect. 5.9. Apply cross-coupled closure to the SEI of Eq. (9.63). Discuss when the additional terms that arise might be important.

9.8. Consideration of interphase mass transport is made complex because the condition of equilibrium, e.g., Eq. (7.112), requires equality of the potential of chemical species. In this chapter, we did not monitor the chemical species. However, we can consider mass transfer between a frozen solid and its melt. For an isothermal case of flow of water through snow, where mass transfer between the solid and fluid can occur, determine the closed equation set where the interface properties can be neglected.

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Chapter 10
Single-fluid-phase Species Transport

10.1 Overview

The goal of this chapter is to extend the macroscale TCAT analysis of Chap. 9 to include compositional effects in single-fluid-phase porous medium systems. Because the development is similar to that employed in the previous chapter, emphasis will be on the extensions to the analysis that are needed.

The formulation will follow the approach of Fig. 9.1. The larger-scale, macroscopic entropy balances and conservation equations are available as described in Chap. 6. In employing these equations, one must make decisions, and declare them in primary restrictions, concerning the refinement of the model in terms of accounting for species dynamics. In general, the option exists to model species mass, momentum, and energy conservation within each system entity based on the equations of Table 6.2. However, here we will demonstrate a hybrid approach that models mass conservation for each species, while considering momentum and energy transport on an entity basis. It is typical in modeling species transport to adopt this hybrid approach. However, within the general framework provided using the TCAT approach, it is possible to model species momentum transport and species energy transport. Modeling of these processes on a species basis carries the burden of a need for additional closure relations.

Larger-scale thermodynamic relations have been developed in Chap. 7. Species-related thermodynamic quantities are needed to account for the states of chemical species within each of the entities. In particular, partial mass thermodynamic functions, including species chemical potentials, as well as the body forces acting on each species will have to be included in the thermodynamic relations. The larger-scale equilibrium conditions in Sect. 7.8 are also employed to provide information about the states of species within an entity and inter-entity relations among potentials. The equilibrium relations contribute to the closure of the conservation equations.

The macroscale evolution equations derived in Chap. 8 are kinematic equations that describe the movement and deformation of entities themselves rather than of

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material in the entities. Although these movements are sometimes related, the evolution of entity shapes does not depend on chemical species. Thus, there are no species-based evolution equations in Chap. 8. Nevertheless, the entity kinematics are important to the overall description of the physical behavior of a system.

The entropy inequality is augmented by the conservation equations and thermodynamic equations to form a constrained entropy inequality. In comparison to augmentation using entity-based equations, species-based conservation equations formulations increase the number of constraints that are imposed. Additionally, the number of Lagrange multipliers in the formulation is also increased. The concomitant extra latitude in specifying the Lagrange multipliers provides a more detailed set of force-flux relations that motivate closure relations. Equilibrium conditions are employed to guide the formulation of a simplified entropy inequality that is composed entirely of force-flux products. The increase in the number of variables due to the monitoring of chemical species movement requires some additional state equations for variables and also additional closure relations. Thus, it is important to count the variables to ensure that the number of conditions is sufficient to produce a closed set of equations. The procedure is the same as that of the last chapter, but the number of variables is significantly larger.

It is worth noting that the results of the present chapter should reduce to those of the previous chapter in the limit when there is only one species present or with summation of a conservation equation over all species. This is important both as a measure of consistency and in assuring that the manipulations required to formulate the problem are not beset with errors. Because a compositional single-fluid-phase system is a superset of a single-fluid-phase system, the latter models can be deduced from the former models by summing over the set of all species. A corollary to this statement is that flow models must be consistent with species transport models. This embedding of information implies that nested, consistent hierarchies of models exist, where certain classes of models can be deduced from more complex hierarchies. One could derive a very complicated model, such as three-fluid-phase flow and species transport in a non-isothermal system with complex solid behavior, and then look at special limiting cases. Instead, we are following an alternative approach of extending model complexity by considering a succession of increasingly more complicated model hierarchies, each with its own intrinsic value and motivating applications. In the last chapter, we considered single-fluid-phase-flow models. Here, we consider single-phase-flow with species transport. Summation of the conservation equations obtained in this chapter will yield a model that is consistent with single-phase-flow models when transport is neglected.

The TCAT analysis of this chapter leads to a model that is an example of a hierarchy of potential models. As is generally the case, the key archival results from the analysis are the CEI and the SEI. These key inequalities provide substantial opportunities for formulation and evaluation of other models in the hierarchy. The elements of the derivation of these key inequalities, as depicted in Fig. 9.1, will be summarized here. Guidance to the steps needed to simplify the complex EI to less challenging forms are provided. We note that the work involved to derive these forms is both long and tedious, but the resultant forms are of considerable value.

10.2 System Definition by Primary Restrictions

The primary restrictions for single-fluid-phase flow that includes species transport in a porous medium system are similar to those from the last chapter when individual species were not considered. The significant difference in stating the primary restrictions is in specifying how compositional effects will be handled. The possibility exists to model mass, momentum, and energy transport of the species on an entity-wide basis. Thus, no differentiation among the species in an entity or consideration of the relative amounts of the species in an entity would be considered. This approach was followed in Chap. 9 using the primary restrictions of Sect. 9.2. Use was made of the conservation equations for entities found in Table 6.3. With the vector momentum equation counted as three components, this approach for single-fluid-phase flow makes use of five mass, momentum, and energy equations for each of the w, s, and ws entities, for a total of 15 conservation equations.

At the other end of the spectrum of possibilities, one could model the transport of mass, momentum, and energy of each species in each entity. This requires the use of conservation equations for species, as found in Table 6.2. If there are N chemical species, each could appear in each of the three entities. Thus, this modeling approach requires that $15N$ conservation equations be used to describe the system. Included in the description would be stress tenors, non-advective heat flux vectors, and so forth for each species in each entity. Thus, significant closure support is required for this large equation set.

As a compromise between the simplicity of the former approach and the detail of the latter approach, one can model some processes on an entity basis and others on a species basis. A first simplification would treat the energy conservation of each entity but make use of momentum and mass conservation for each chemical species. Thus, each entity would make use of one energy equation, $3N$ momentum equations, and N mass conservation equations. For the single-fluid-phase system with two phase entities and one interface entity, $12N+3$ conservation equations would describe the system [3]. Because the velocity of each chemical species is solved for in a momentum equation, there is no need for closure of intraphase dispersion in the species mass conservation equation in this formulation.

A second, even simpler, compromise poses both the energy and momentum conservation equations on an entity basis but considers mass conservation for each species in each entity [3]. Thus, each entity is described by $N+4$ conservation equations such that the three-entity system is modeled using $3N+12$ conservation equations. With this approach, because entity velocities rather than species velocities are described in the momentum equation, it is necessary to make use of a dispersion velocity relative to the entity velocity in the mass conservation equations. Closure relations are needed for the dispersion velocities.

The choice among the two extreme situations and the two compromises is made in the statement of the primary restrictions to be employed. It is important that this selection be made prior to using the conservation equations to augment the entropy inequality because the forms these equations take depend on the refinement selected. For example, when the species dispersion vectors appear in the mass conservation equation, they should appear explicitly in the momentum and energy equations rather than implicitly in some quantity obtained by summing over the species momentum equations, as with the variables in Table 6.3.

The primary restrictions employed here for modeling species transport in a single-fluid-phase porous medium system are analogous to Primary Restrictions 9.1–9.3 as follows:

Primary Restriction 10.1 (System and Scale)
The system of concern consists of a single fluid phase w, a relatively immobile solid phase s, and an interface ws between the two phases. The phases and interfaces are composed of N chemical species that may react and transfer between the phases and the interface. The spatial scale of concern is the macroscale, ℓ^{ma}, *with* $\ell^{\mathrm{r}}_{\mathrm{r}} \ll \ell^{\mathrm{ma}} \ll \ell^{\mathrm{me}}$ *where* $\ell^{\mathrm{r}}_{\mathrm{r}}$ *and* ℓ^{me} *are the resolution scale and megascale of the system, respectively.*[1] *The domain of the system is* Ω *with boundary* Γ*.*

Primary Restriction 10.2 (Phenomena Modeled)
The phenomena of concern consist of the transport of mass, momentum, and energy in each of the entities. Transport phenomena of various chemical species within an entity and between entities will be modeled explicitly using mass conservation equations for each species. The momentum and energy of the entities will be modeled using entity-based equations.

Primary Restriction 10.3 (Thermodynamic Theory)
Classical irreversible thermodynamics (CIT) is employed to describe the thermodynamic behavior of the system entities at equilibrium and near-equilibrium states. The solid phase is modeled as elastic.

These restrictions impose the same limitations, and allow for the same flexibility, in modeling as described in the last chapter with one major exception. The addition of species transport here will result in a model capable of describing the distribution of advecting, reacting, and dispersing chemical constituents throughout the system. Modeling of the chemical constituents will be accomplished making use of mass conservation equations for each species in each entity. The species momentum and energy will not be solved for directly using conservation equations but can be estimated in hindsight from a model making use of constitutive expressions for the dispersion velocity, thermodynamic relations, and knowledge of state variables.

With the primary restrictions stated, we turn our attention to selection of the appropriate set of conservation and thermodynamic equations for use in describing the system. The approach parallels that of the last chapter, but we have to incorporate species properties and processes consistently. The next section highlights the considerations which dictate appropriate equation forms that satisfy the system described by the primary restrictions.

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[1] The descriptions of length scales are provided in the discussion of Eq. (1.1).

10.3 Constrained Entropy Inequality

The procedure for deriving the constrained entropy inequality has been demonstrated for a microscale analysis of a fluid phase in Sect. 5.4 and for macroscale single-phase flow in a porous medium in Sect. 9.4. The same approach will be followed here. The general idea is to constrain the entropy inequality with conservation and thermodynamic equations so that the entropy generation can be expressed as a sum of products of force-flux pairs. The elements of the approach will be outlined here for the case as defined by the primary restrictions.

10.3.1 Augmented Entropy Inequality

The general form of the augmented entropy inequality (AEI) was given in Eq. (9.18). This form is a useful starting point for constraining the entropy inequality in any macroscale TCAT analysis. This equation is repeated here with

$$\begin{aligned}
&\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\mathcal{S}_*^{\overline{\overline{i\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda_{\mathcal{E}}^{i\alpha}\mathcal{E}_*^{\overline{\overline{i\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{i\alpha}\cdot\boldsymbol{\mathcal{P}}_*^{\overline{\overline{i\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda_{\mathcal{M}}^{i\alpha}\mathcal{M}_*^{\overline{\overline{i\alpha}}}\\
&\quad+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda_{\mathcal{G}}^{i\alpha}\mathcal{G}_*^{\overline{\overline{i\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda_{\mathcal{T}}^{i\alpha}\mathcal{T}_*^{\overline{\overline{i\alpha}}}\\
&\quad+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda_{\mathcal{T}\mathcal{G}}^{i\alpha}\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}}=\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\Lambda^{\overline{\overline{i\alpha}}}\geq 0\,,
\end{aligned}\tag{10.1}$$

where the quantities with the subscript $*$ are species-based conservation and balance equations from Table 6.2 and thermodynamic relations from Table 7.2. The λ coefficients are Lagrange multipliers whose values are determined in part by the primary restrictions and in part by their function in eliminating time derivatives from the equation.

Primary restriction 10.2 indicates that species transport will be explicitly considered in the mass conservation equations but will be accounted for only implicitly in modeling momentum and energy. This restriction is applied in Eq. (10.1) by allowing the Lagrange multiplier for mass conservation, $\lambda_{\mathcal{M}}^{i\alpha}$, to retain its dependence on the chemical species being considered while requiring all other Lagrange multipliers to be independent of species. Because the Lagrange multipliers all multiply quantities that are equal to zero, they can be selected arbitrarily to obtain a desired form of the entropy inequality. Imposition of the stated conditions on the Lagrange multipliers allows Eq. (10.1) to be modified to

$$\sum_{\alpha\in\mathfrak{I}}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{S}_*^{\overline{\overline{i\alpha}}}\right)+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{E}}^{\alpha}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{E}_*^{\overline{\overline{i\alpha}}}\right)+\sum_{\alpha\in\mathfrak{I}}\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{\alpha}\cdot\left(\sum_{i\in\mathfrak{I}_s}\boldsymbol{\mathcal{P}}_*^{\overline{\overline{i\alpha}}}\right)$$

$$+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda_{\mathcal{M}}^{i\alpha}\mathcal{M}_*^{\overline{\overline{i\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{G}}^{\alpha}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{G}_*^{\overline{\overline{i\alpha}}}\right)+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{T}}^{\alpha}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{T}_*^{\overline{\overline{i\alpha}}}\right)$$
$$+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{TG}}^{\alpha}\left(\sum_{i\in\mathfrak{I}_s}\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{i\alpha}}}\right)=\sum_{\alpha\in\mathfrak{I}}\left(\sum_{i\in\mathfrak{I}_s}\Lambda^{\overline{\overline{i\alpha}}}\right)\geq 0\,. \tag{10.2}$$

One might think that the next step is to sum the species-based equations appearing in Table 6.2 that are unencumbered by a Lagrange multiplier over the species to obtain equations appearing in Table 6.3. For example, we can obtain $\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$ as the sum of $\boldsymbol{\mathcal{P}}_*^{\overline{\overline{i\alpha}}}$ over all species. However, this approach does not explicitly take into account the dispersive velocities of the chemical species.

The issue at hand can perhaps be illuminated by recalling that Eq. (6.74), the species mass conservation equation written in terms of the entity velocity $\mathbf{v}^{\overline{\alpha}}$ and the dispersive velocity, $\mathbf{u}^{\overline{\overline{i\alpha}}}$, was obtained because the species velocity, $\mathbf{v}^{\overline{i\alpha}}$, is equal to $\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}$. Thus, $\mathcal{M}_*^{\overline{\overline{i\alpha}}}$ was converted to a form identified as $\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$ where

$$\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}=\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}+\nabla\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right)$$
$$-\epsilon^{\overline{\overline{\alpha}}}r^{i\alpha}-\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}}\overset{i\kappa\to i\alpha}{M}=0\quad\text{for } i\in\mathfrak{I}_s,\alpha\in\mathfrak{I}\,. \tag{10.3}$$

Three features of this equation are particularly noteworthy. First, the dispersive velocity appears explicitly and must be accounted for. Second, chemical reactions are included in the equation. Third, the inter-entity exchange is expressed in terms of chemical species rather than on an entity basis. Although Eq. (10.3) makes use of the entity-based velocity, the features noted make this equation distinctly different from the entity-based mass conservation equation as employed in the last chapter. To ensure that the featured processes are modeled in the TCAT framework, it is important that they appear explicitly in the other conservation equations rather than be consolidated into entity properties and processes as was done in obtaining the equations of Table 6.3. Thus, the summation over species-based equations in parentheses in Eq. (10.1) is performed as indicated, but the combination of the summed terms is done to facilitate incorporation of the effects of dispersion into the model.

Table 10.1 provides a key for all relations between an entry in Eq. (10.2) and the form of the equation that is used for the current case of dispersion modeling. The replacement groups are exactly equivalent to the precursors. The important feature is the way the quantities are combined in defining variables. Making use of the quantities identified in Table 10.1, Eq. (10.2) becomes

$$\sum_{\alpha\in\mathfrak{I}}\mathcal{S}_{**}^{\overline{\overline{\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{E}}^{\alpha}\mathcal{E}_{**}^{\overline{\overline{\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{\alpha}\cdot\boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda_{\mathcal{M}}^{i\alpha}\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$$
$$+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{G}}^{\alpha}\mathcal{G}_{**}^{\overline{\overline{\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{T}}^{\alpha}\mathcal{T}_{*}^{\overline{\overline{\alpha}}}+\sum_{\alpha\in\mathfrak{I}}\lambda_{\mathcal{TG}}^{\alpha}\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}=\sum_{\alpha\in\mathfrak{I}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. \tag{10.4}$$

Table 10.1 Forms of the entries in Eq. (10.2) that are used to state the augmented entropy inequality. Replacement notation is provided and the equation number is given that is the source of terms that appear in the expanded equation

Quantity	Entry	Replacement	Source
Entropy	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{S}_*^{\overline{\overline{i\alpha}}}$	$\mathcal{S}_{**}^{\overline{\overline{\alpha}}}$	Eq. (6.195)
Energy	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{E}_*^{\overline{\overline{i\alpha}}}$	$\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$	Eq. (6.203)
Momentum	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{P}_*^{\overline{\overline{i\alpha}}}$	$\mathcal{P}_{**}^{\overline{\overline{\alpha}}}$	Eq. (6.201)
Mass	$\mathcal{M}_*^{\overline{\overline{i\alpha}}}$	$\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$	Eq. (6.74)
Force Potential	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{G}_*^{\overline{\overline{i\alpha}}}$	$\mathcal{G}_{**}^{\overline{\overline{\alpha}}}$	Eq. (6.197)
Fluid Thermodynamics	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{T}_*^{\overline{\overline{iw}}}$	$\mathcal{T}_*^{\overline{\overline{w}}}$	Eq. (7.54)
Solid Thermodynamics	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{T}_*^{\overline{\overline{is}}}$	$\mathcal{T}_*^{\overline{\overline{s}}}$	Eq. (7.80)
Interface Thermodynamics	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{T}_*^{\overline{\overline{iws}}}$	$\mathcal{T}_*^{\overline{\overline{ws}}}$	Eq. (7.96)
Fluid Potential Energy	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{iw}}}$	$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{w}}}$	Eq. (7.58)
Solid Potential Energy	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{is}}}$	$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{s}}}$	Eq. (7.81)
Interface Potential Energy	$\sum\limits_{i\in\mathfrak{I}_s} \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{iws}}}$	$\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$	Eq. (7.97)
Entropy Generation	$\sum\limits_{i\in\mathfrak{I}_s} \Lambda^{\overline{\overline{i\alpha}}}$	$\Lambda^{\overline{\overline{\alpha}}}$	Eq. (6.149)

This equation is the appropriate augmented inequality for modeling transport of N chemical species in a single-fluid-phase porous medium system such that $\mathfrak{I} = \{w, s, ws\}$ and $\mathfrak{I}_s = \{1, \ldots, N\}$ using a species-based mass conservation equation in conjunction with all other conservation, balance, and thermodynamic equations formulated on an entity basis.

10.3.2 Determination of Lagrange Multipliers

The goal of the selection of Lagrange multipliers is to eliminate as many material derivatives as possible, so that the entropy generation will be in terms of force-flux products. The material derivative forms are thus key elements that appear in Eq. (10.4). We expand this equation by explicitly inserting the material derivatives while indicating the presence of additional terms using ellipses. The resulting equation is

$$
\begin{aligned}
&\sum_{\alpha\in\mathcal{I}}\left(\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\dots\right)\\
&+\sum_{\alpha\in\mathcal{I}}\lambda_{\mathcal{E}}^{\alpha}\left(\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left\{E^{\overline{\overline{\alpha}}}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left[\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+\sum_{i\in\mathcal{I}_s}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\right\}+\dots\right)\\
&+\sum_{\alpha\in\mathcal{I}}\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{\alpha}\cdot\left[\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}})}{\mathrm{D}t}+\dots\right]+\sum_{\alpha\in\mathcal{I}}\sum_{i\in\mathcal{I}_s}\lambda_{\mathcal{M}}^{i\alpha}\left[\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}+\dots\right]\\
&+\sum_{\alpha\in\mathcal{I}}\lambda_{\mathcal{G}}^{\alpha}\left(\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\dots\right)\\
&+\sum_{\alpha\in\mathcal{I}}\lambda_{\mathcal{T}}^{\alpha}\left[\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\theta^{\overline{\overline{\alpha}}}\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\sum_{i\in\mathcal{I}_s}\mu^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}+\dots\right]\\
&+\sum_{\alpha\in\mathcal{I}}\lambda_{\mathcal{TG}}^{\alpha}\left[\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\sum_{i\in\mathcal{I}_s}\psi^{\overline{i\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}+\dots\right]=\sum_{\alpha\in\mathcal{I}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. \qquad (10.5)
\end{aligned}
$$

The material derivatives in this expression can be expanded using the product rule so that terms can be combined. Additionally, we make use of the fact that

$$
\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t}=\sum_{i\in\mathcal{I}_s}\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}\,. \qquad (10.6)
$$

The full set of unique material derivatives is the set $\mathcal{D}$, where

$$
\mathcal{D}=\left\{\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}}{\mathrm{D}t},\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right),\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}\right\}
$$
$$
\text{for } \alpha\in\mathcal{I}, i\in\mathcal{I}_s\,. \qquad (10.7)
$$

Rearrangement of Eq. (10.5) so that it is expressed as coefficients multiplying the unique derivatives, with the additional terms accounted for by a single ellipsis, yields

$$
\sum_{\alpha\in\mathcal{I}}\left(1-\theta^{\overline{\overline{\alpha}}}\lambda_{\mathcal{T}}^{\alpha}\right)\frac{\mathrm{D}^{\overline{\alpha}}\eta^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\sum_{\alpha\in\mathcal{I}}\left(\lambda_{\mathcal{E}}^{\alpha}+\lambda_{\mathcal{T}}^{\alpha}\right)\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}
$$

$$
\begin{aligned}
&+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\left[\lambda_{\mathcal{E}}^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)+\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{\alpha}\cdot\mathbf{v}^{\overline{\alpha}}+\lambda_{\mathcal{M}}^{i\alpha}\right.\\
&\qquad\qquad\left.-\lambda_{\mathcal{T}}^{\alpha}\mu^{\overline{i\alpha}}-\lambda_{\mathcal{T}\mathcal{G}}^{\alpha}\psi^{\overline{i\alpha}}\right]\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}})}{\mathrm{D}t}\\
&+\sum_{\alpha\in\mathfrak{I}}\left(\lambda_{\mathcal{E}}^{\alpha}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}+\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{\alpha}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\right)\cdot\frac{\mathrm{D}^{\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}}{\mathrm{D}t}\\
&+\sum_{\alpha\in\mathfrak{I}}\sum_{i\in\mathfrak{I}_s}\lambda_{\mathcal{E}}^{\alpha}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\\
&+\sum_{\alpha\in\mathfrak{I}}\left(\lambda_{\mathcal{G}}^{\alpha}+\lambda_{\mathcal{T}\mathcal{G}}^{\alpha}\right)\frac{\mathrm{D}^{\overline{\alpha}}\Psi^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\cdots=\sum_{\alpha\in\mathfrak{I}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,.
\end{aligned}
\tag{10.8}
$$

With vectors counted as contributing three elements, there are $18+6N$ material derivatives in this equation and $21+3N$ Lagrange multiplier coefficients. The time derivative of $K_E^{\overline{\overline{i\alpha}}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}/2$ cannot be eliminated from this equation except by selection of the trivial value $\lambda_{\mathcal{E}}^{\alpha}=0$. Thus, if these $3N$ terms are excluded from further consideration, the number of derivatives remaining is $18+3N$ leaving an excess of 3 Lagrange multipliers that can be specified arbitrarily. If we select $\lambda_{\mathcal{T}}^{\alpha}=\lambda_{\mathcal{T}\mathcal{G}}^{\alpha}$ for $\alpha\in\mathfrak{I}$, we can see from Eq. (10.5) that we are essentially combining $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$ into a single thermodynamic relation that includes gravitational effects.[2] Solution for the remaining Lagrange multipliers such that the coefficients of the time derivatives are zero yields

$$\lambda_{\mathcal{T}}^{\alpha}=\lambda_{\mathcal{T}\mathcal{G}}^{\alpha}=\frac{1}{\theta^{\overline{\overline{\alpha}}}}\,, \tag{10.9}$$

$$\lambda_{\mathcal{E}}^{\alpha}=\lambda_{\mathcal{G}}^{\alpha}=-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\,, \tag{10.10}$$

$$\boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{\alpha}=\frac{\mathbf{v}^{\overline{\alpha}}}{\theta^{\overline{\overline{\alpha}}}}\,, \tag{10.11}$$

and

$$\lambda_{\mathcal{M}}^{i\alpha}=\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{i\alpha}}+\psi^{\overline{i\alpha}}-\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\,, \tag{10.12}$$

where $\alpha\in\mathfrak{I}$ and $i\in\mathfrak{I}_s$. Comparison of these results with Eqs. (9.25)–(9.30) indicates that the addition of dispersion to the problem does not impact the expressions for the Lagrange multipliers for the momentum, energy, and thermodynamic equations.

The particular values of the Lagrange multipliers are substituted back into the AEI, Eq. (10.4). With the conservation and balance equations identified in Table

---

[2] As a consequence of this selection, it is subsequently seen that $\lambda_{\mathcal{G}}^{\alpha}=\lambda_{\mathcal{E}}^{\alpha}$ such that the energy and potential energy equations are essentially added together as well.

10.1 inserted and the time derivatives cancelled, the result without any additional rearrangement of terms is

$$
\begin{aligned}
&\sum_{\alpha\in\mathfrak{J}}\left[\eta^{\overline{\overline{\alpha}}}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}b^{\alpha}-\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\overset{i\kappa\to i\alpha}{M}\,\overline{\eta}_i^{\overline{\overline{\alpha,\kappa}}}-\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{\kappa\to\alpha}{\Phi_0}-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}\right)\right] && \mathcal{S}_{**}^{\overline{\overline{\alpha}}}\\
&-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\frac{\mathrm{D}^{\overline{\alpha}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right] && \mathcal{E}_{**}^{\overline{\overline{\alpha}}}\\
&-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left\{E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left[\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+\sum_{i\in\mathfrak{J}_s}\omega^{i\overline{\alpha}}\left(K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\right]\right\}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}} && \mathcal{E}_{**}^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}})+\varepsilon^{\overline{\overline{\alpha}}}h_0^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}h^{\alpha}\right] && \mathcal{E}_{**}^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}+\frac{\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)}{2}\right. && \mathcal{E}_{**}^{\overline{\overline{\alpha}}}\\
&\qquad\qquad\left.+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}\right] && \mathcal{E}_{**}^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{\kappa\to\alpha}{Q_1}\right] && \mathcal{E}_{**}^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right) && \mathcal{E}_{**}^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\mathbf{v}^{\overline{\alpha}}\cdot\left[\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\right. && \boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}\\
&\qquad\qquad\left.-\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\overset{i\kappa\to i\alpha}{M}\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\right] && \boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}\\
&-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\mathbf{v}^{\overline{\alpha}}\cdot\overset{\kappa\to\alpha}{\mathbf{T}_0}-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\mathbf{v}^{\overline{\alpha}}\cdot\left[\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right)\right] && \boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left(\mu^{\overline{i\alpha}}+\psi^{\overline{i\alpha}}-\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\left[\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}\right. && \mathcal{M}_{**}^{\overline{\overline{i\alpha}}}\\
&\qquad\qquad\left.+\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right)-\varepsilon^{\overline{\overline{\alpha}}}r^{i\alpha}-\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{i\kappa\to i\alpha}{M}\right] && \mathcal{M}_{**}^{\overline{\overline{i\alpha}}}\\
&-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left\{\Psi^{\overline{\overline{\alpha}}}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}+\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{g}^{\overline{i\alpha}}\cdot\left(\mathbf{v}^{\overline{\alpha}}+\mathbf{u}^{\overline{\overline{i\alpha}}}\right)+\varepsilon^{\overline{\overline{\alpha}}}h_0^{\overline{\overline{\alpha}}}\right. && \mathcal{G}_{**}^{\overline{\overline{\alpha}}}
\end{aligned}
$$

$$
\begin{aligned}
&\qquad - \sum_{\kappa\in\mathfrak{I}_{c\alpha}} \sum_{i\in\mathfrak{I}_s} \overset{i\kappa\to i\alpha}{M} \psi_i^{\overline{\overline{\alpha,\kappa}}} - \sum_{\kappa\in\mathfrak{I}_{c\alpha}} \overset{\kappa\to\alpha}{G_0} && \mathcal{G}_{**}^{\overline{\overline{\alpha}}} \\
&\qquad - \nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}} - \sum_{i\in\mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\psi^{\overline{i\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right) && \mathcal{G}_{**}^{\overline{\overline{\alpha}}} \\
&\qquad - \sum_{i\in\mathfrak{I}_s} \left\langle \rho_\alpha\omega_{i\alpha}\left[\frac{\partial^{(n)}\psi_{i\alpha}}{\partial t} + \mathbf{v}_{i\alpha}\cdot\left(\mathsf{I}-\mathsf{I}_{\alpha}^{(n)}\right)\cdot\mathbf{g}_{i\alpha}\right]\right\rangle_{\Omega_\alpha,\Omega} && \mathcal{G}_{**}^{\overline{\overline{\alpha}}} \\
&\qquad - \left.\sum_{i\in\mathfrak{I}_s} \langle r_{i\alpha}\psi_{i\alpha}\rangle_{\Omega_\alpha,\Omega}\right\} && \mathcal{G}_{**}^{\overline{\overline{\alpha}}} \\
&+ \frac{1}{\theta^{\overline{\overline{w}}}}\left\langle \mathbf{n}_w\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)p_w\right\rangle_{\Omega_{ws},\Omega} && \mathcal{T}_{*}^{\overline{\overline{w}}} \\
&+ \frac{1}{\theta^{\overline{\overline{w}}}}\left[\left\langle \eta_w\frac{\mathrm{D}^{\overline{s}}(\theta_w-\theta^{\overline{\overline{w}}})}{\mathrm{D}t}\right\rangle_{\Omega_w,\Omega} + \sum_{i\in\mathfrak{I}_s}\left\langle \rho_w\omega_{iw}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{iw}-\mu^{\overline{iw}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_w,\Omega}\right] && \mathcal{T}_{*}^{\overline{\overline{w}}} \\
&- \frac{1}{\theta^{\overline{\overline{w}}}}\left[\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}} - \nabla(\varepsilon^{\overline{\overline{w}}}p^{w}) + \sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\nabla\mu^{\overline{iw}}\right]\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right) && \mathcal{T}_{*}^{\overline{\overline{w}}} \\
&- \frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot(\mathbf{v}_{ws}-\mathbf{v}_s)\,\boldsymbol{\sigma}_s{:}\frac{\mathsf{C}_s}{j_s}\right\rangle_{\Omega_{ws},\Omega} && \mathcal{T}_{*}^{\overline{\overline{s}}} \\
&- \frac{1}{\theta^{\overline{\overline{s}}}}\left[\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} - \left\langle \eta_s\frac{\mathrm{D}^{\overline{s}}(\theta_s-\theta^{\overline{\overline{s}}})}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}\right] && \mathcal{T}_{*}^{\overline{\overline{s}}} \\
&+ \frac{1}{\theta^{\overline{\overline{s}}}}\left[\sum_{i\in\mathfrak{I}_s}\left\langle \rho_s\omega_{is}\frac{\mathrm{D}^{\overline{s}}(\mu_{is}-\mu^{\overline{is}})}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}\right. && \mathcal{T}_{*}^{\overline{\overline{s}}} \\
&\qquad \left. - \nabla\cdot\left\langle\left[\mathsf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathsf{C}_s}{j_s}\mathsf{I}\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right] && \mathcal{T}_{*}^{\overline{\overline{s}}} \\
&- \frac{1}{\theta^{\overline{\overline{s}}}}\left[\varepsilon^{\overline{\overline{s}}}\mathsf{t}^{s}{:}\mathsf{d}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}}\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\frac{\mathsf{C}^{s}}{j^{s}}\mathsf{I}{:}\mathsf{d}^{\overline{\overline{s}}} - \left\langle\left(\nabla\cdot\mathsf{t}_s-\nabla\boldsymbol{\sigma}_s{:}\frac{\mathsf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right] && \mathcal{T}_{*}^{\overline{\overline{s}}} \\
&+ \frac{1}{\theta^{\overline{\overline{ws}}}}\left[\left\langle \eta_{ws}\frac{\mathrm{D}'^{\overline{s}}(\theta_{ws}-\theta^{\overline{\overline{ws}}})}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega}\right. && \mathcal{T}_{*}^{\overline{\overline{ws}}} \\
&\qquad \left. + \sum_{i\in\mathfrak{I}_s}\left\langle \rho_{ws}\omega_{iws}\frac{\mathrm{D}'^{\overline{s}}(\mu_{iws}-\mu^{\overline{iws}})}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega}\right] && \mathcal{T}_{*}^{\overline{\overline{ws}}} \\
&- \frac{1}{\theta^{\overline{\overline{ws}}}}\left[\eta^{\overline{\overline{ws}}}\nabla\theta^{\overline{\overline{ws}}} + \nabla\cdot\left\langle\mathsf{I}'_{ws}\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega} + \sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{\overline{ws}}}\nabla\mu^{\overline{iws}}\right]\cdot\left(\mathbf{v}^{\overline{\overline{ws}}}-\mathbf{v}^{\overline{s}}\right) && \mathcal{T}_{*}^{\overline{\overline{ws}}} \\
&+ \frac{1}{\theta^{\overline{\overline{ws}}}}\left[\nabla\cdot\left\langle\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{\overline{ws}}}\right)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega} + \left\langle\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}{:}\mathsf{d}^{\overline{\overline{ws}}}\right] && \mathcal{T}_{*}^{\overline{\overline{ws}}}
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \nabla'\cdot\mathbf{l}'_{ws}\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega} && \mathcal{T}_{*}^{\overline{\overline{ws}}}\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \eta_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\theta^{\overline{\overline{ws}}} && \mathcal{T}_{*}^{\overline{\overline{ws}}}\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\sum_{i\in\mathfrak{J}_s}\left\langle \rho_{ws}\omega_{iws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\mu^{\overline{iws}} && \mathcal{T}_{*}^{\overline{\overline{ws}}}\\
&-\frac{1}{\theta^{\overline{\overline{w}}}}\sum_{i\in\mathfrak{J}_s}\left[\left\langle \rho_{w}\omega_{iw}\frac{\mathrm{D}^{\overline{s}}\psi^{\overline{iw}}}{\mathrm{D}t}\right\rangle_{\Omega_{w},\Omega}+\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)\cdot\nabla\psi^{\overline{iw}}\right] && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{w}}}\\
&-\frac{1}{\theta^{\overline{\overline{s}}}}\sum_{i\in\mathfrak{J}_s}\left\langle \rho_{s}\omega_{is}\frac{\mathrm{D}^{\overline{s}}\psi^{\overline{is}}}{\mathrm{D}t}\right\rangle_{\Omega_{s},\Omega} && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{s}}}\\
&-\frac{1}{\theta^{\overline{\overline{ws}}}}\sum_{i\in\mathfrak{J}_s}\left[\left\langle \rho_{ws}\omega_{iws}\frac{\mathrm{D}'^{\overline{s}}\psi^{\overline{iws}}}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega}+\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\nabla\psi^{\overline{iws}}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\right] && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\sum_{i\in\mathfrak{J}_s}\left\langle \rho_{ws}\omega_{iws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{l}-\mathbf{l}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\psi^{\overline{iws}} && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}\\
&=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. && \mathcal{S}_{**}^{\overline{\overline{\alpha}}}
\end{aligned}
\tag{10.13}
$$

The designation of an equation at the far right of each line in Eq. (10.13) indicates the conservation, balance, or thermodynamic equation that is the source for the terms appearing in the line.

10.3.3 Formulation of the CEI

Some insights into the types of manipulations needed to rearrange terms in Eq. (10.13) to obtain a CEI were given in Sect. 9.4.4 and Sect. C.1. In Sect. 9.4.5 some additional thoughts were provided in regard to using the equilibrium relations to drive the combination of terms toward a force-flux form. The considerations of those sections apply here as well.

Table 10.2 is a broad roadmap and abbreviated guide for rearranging terms in Eq. (10.13) to obtain the CEI, Eq. (10.14). From the table it can be seen that the constraint equations, in combination with the Lagrange multipliers, work in concert to provide the force-flux forms. The reader interested in more extensive details of the manipulations performed in deriving Eq. (10.14) is referred to Sect. C.2.

Rearrangement of Eq. (10.13) in light of the guidance from Table 10.2 and as specified in Sect. C.2 provides the constrained entropy inequality given by

Table 10.2 CEI formulation summary for the derivation of Eq. (10.14), where the operation abbreviations represent A for addition and subtraction, E for Euler equation identity, I for identity tensor components as shown in Eq. (9.41), O for objective form, and P for the product rule, and the general entity qualifier α implies all entities unless otherwise noted

Line(s)	Force	Precursor Equation(s)	Operations
1–5	—	$\mathcal{S}_{**}^{\overline{\overline{\alpha}}}, \boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}, \mathcal{E}_{**}^{\overline{\overline{\alpha}}}, \mathcal{G}_{**}^{\overline{\overline{\alpha}}}, \mathcal{T}_{*}^{\overline{\overline{\alpha}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$	O,A
6–10	—	$\mathcal{S}_{**}^{\overline{\overline{\alpha}}}, \mathcal{M}_{**}^{\overline{\overline{i\alpha}}}, \mathcal{E}_{**}^{\overline{\overline{\alpha}}}, \mathcal{G}_{**}^{\overline{\overline{\alpha}}}, \mathcal{T}_{*}^{\overline{\overline{s}}}$	P
11–12	$\mathbf{d}^{\overline{\overline{\alpha}}}$	$\mathcal{S}_{**}^{\overline{\overline{\alpha}}}, \mathcal{M}_{**}^{\overline{\overline{i\alpha}}}, \boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}, \mathcal{E}_{**}^{\overline{\overline{\alpha}}}, \mathcal{T}_{*}^{\overline{\overline{s}}}, \mathcal{T}_{*}^{\overline{\overline{ws}}}$	E,P
13–16	$\nabla\left(\dfrac{1}{\theta^{\overline{\overline{\alpha}}}}\right)$	$\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}, \mathcal{E}_{**}^{\overline{\overline{\alpha}}}, \mathcal{G}_{**}^{\overline{\overline{\alpha}}}, \mathcal{T}_{*}^{\overline{\overline{s}}}$	P
17–18	$\nabla\Bigg[\left(\mu^{\overline{i\alpha}} + K_E^{\overline{\overline{i\alpha}}} + \dfrac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2} + \psi^{\overline{i\alpha}}\right)$ $-\left(\mu^{\overline{N\alpha}} + K_E^{\overline{\overline{N\alpha}}} + \dfrac{\mathbf{u}^{\overline{\overline{N\alpha}}}\cdot\mathbf{u}^{\overline{\overline{N\alpha}}}}{2} + \psi^{\overline{N\alpha}}\right)\Bigg]$	$\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$	P
19–20	—	$\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}, \mathcal{G}_{**}^{\overline{\overline{\alpha}}}$	—
21–22	$\dfrac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{iw}} + K_E^{\overline{\overline{iw}}} + \dfrac{\mathbf{u}^{\overline{\overline{iw}}}\cdot\mathbf{u}^{\overline{\overline{iw}}}}{2} + \psi^{\overline{iw}}\right)$ $-\dfrac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{iws}} + K_E^{\overline{\overline{iws}}} + \dfrac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2} + \psi^{\overline{iws}}\right)$	$\mathcal{M}_{**}^{\overline{\overline{iw}}}, \mathcal{M}_{**}^{\overline{\overline{iws}}}$	—
23–24	$\dfrac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{is}} + K_E^{\overline{\overline{is}}} + \dfrac{\mathbf{u}^{\overline{\overline{is}}}\cdot\mathbf{u}^{\overline{\overline{is}}}}{2} + \psi^{\overline{is}} + \dfrac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^s}{3\rho^s j^s}\right)$ $-\dfrac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{iws}} + K_E^{\overline{\overline{iws}}} + \dfrac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2} + \psi^{\overline{iws}}\right)$	$\mathcal{M}_{**}^{\overline{\overline{is}}}, \mathcal{M}_{**}^{\overline{\overline{iws}}}, \mathcal{T}_{*}^{\overline{\overline{s}}}$	A
25	—	$\mathcal{T}_{*}^{\overline{\overline{s}}}$	A,I
26–28	$\dfrac{1}{\theta^{\overline{\overline{w}}}} - \dfrac{1}{\theta^{\overline{\overline{ws}}}}$	$\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}, \mathcal{E}_{**}^{\overline{\overline{\alpha}}}, \mathcal{G}_{**}^{\overline{\overline{\alpha}}}, \mathcal{T}_{*}^{\overline{\overline{w}}}\ \alpha \in \{w, ws\}$	A,O
29–31	$\dfrac{1}{\theta^{\overline{\overline{s}}}} - \dfrac{1}{\theta^{\overline{\overline{ws}}}}$	$\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}, \mathcal{E}_{**}^{\overline{\overline{\alpha}}}, \mathcal{G}_{**}^{\overline{\overline{\alpha}}}, \mathcal{T}_{*}^{\overline{\overline{s}}}\ \alpha \in \{s, ws\}$	A,O
32–35	$\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}$	$\mathcal{M}_{**}^{\overline{\overline{iw}}}, \boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{w}}}, \mathcal{E}_{**}^{\overline{\overline{w}}}, \mathcal{G}_{**}^{\overline{\overline{w}}}, \mathcal{T}_{*}^{\overline{\overline{w}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{w}}}$	A,O
36–42	$\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}$	$\mathcal{M}_{**}^{\overline{\overline{iws}}}, \boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{ws}}}, \mathcal{E}_{**}^{\overline{\overline{ws}}}, \mathcal{G}_{**}^{\overline{\overline{ws}}}, \mathcal{T}_{*}^{\overline{\overline{ws}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$	A,O
43–44	—	$\mathcal{G}_{**}^{\overline{\overline{ws}}}, \mathcal{T}_{*}^{\overline{\overline{\alpha}}}$	A,I
45	—	$\mathcal{T}_{*}^{\overline{\overline{s}}}$	I
46	—	$\mathcal{T}_{*}^{\overline{\overline{s}}}$	—
47	—	$\mathcal{T}_{*}^{\overline{\overline{ws}}}$	A
48	—	$\mathcal{T}_{*}^{\overline{\overline{ws}}}$	—
49–50	—	$\mathcal{E}_{**}^{\overline{\overline{ws}}}, \mathcal{T}_{*}^{\overline{\overline{ws}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$	A,O
51	—	$\mathcal{S}_{*}^{\overline{\overline{\alpha}}}$	—

$$
\begin{aligned}
&-\sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\Biggl\{\varepsilon^{\overline{\overline{\alpha}}}b^{\alpha}-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\Biggl[\varepsilon^{\overline{\overline{\alpha}}}h^{\alpha}+\Biggl\langle\eta_{\alpha}\frac{\mathrm{D}^{\overline{s}}\left(\theta_{\alpha}-\theta^{\overline{\overline{\alpha}}}\right)}{\mathrm{D}t}\Biggr\rangle_{\Omega_{\alpha},\Omega}\\
&\qquad+\sum_{i\in\mathfrak{I}_s}\Biggl\langle\rho_{\alpha}\omega_{i\alpha}\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\Biggl(\mu_{i\alpha}+\psi_{i\alpha}-\mu^{\overline{i\alpha}}-K_E^{\overline{\overline{i\alpha}}}-\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}-\psi^{\overline{i\alpha}}\Biggr)\Biggr\rangle_{\Omega_{\alpha},\Omega}\Biggr]\Biggr\}\\
&-\Biggl\{\varepsilon^{\overline{\overline{ws}}}b^{ws}-\frac{1}{\theta^{\overline{\overline{ws}}}}\Biggl[\varepsilon^{\overline{\overline{ws}}}h^{ws}+\Biggl\langle\eta_{ws}\frac{\mathrm{D}'^{\overline{s}}\left(\theta_{ws}-\theta^{\overline{\overline{ws}}}\right)}{\mathrm{D}t}\Biggr\rangle_{\Omega_{ws},\Omega}\\
&\qquad+\sum_{i\in\mathfrak{I}_s}\Biggl\langle\rho_{ws}\omega_{iws}\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t}\Biggl(\mu_{iws}+\psi_{iws}-\mu^{\overline{iws}}\\
&\qquad\qquad-K_E^{\overline{\overline{iws}}}-\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}-\psi^{\overline{iws}}\Biggr)\Biggr\rangle_{\Omega_{ws},\Omega}\Biggr]\Biggr\}\\
&-\sum_{\alpha\in\mathfrak{I}_{/S}}\nabla\cdot\Biggl\{\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\Biggl[\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}}\\
&\qquad+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\Biggl(\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\Biggr)\mathbf{u}^{\overline{\overline{i\alpha}}}\Biggr]\Biggr\}\\
&-\nabla\cdot\Biggl\{\varepsilon^{\overline{\overline{s}}}\boldsymbol{\varphi}^{\overline{\overline{s}}}-\frac{1}{\theta^{\overline{\overline{s}}}}\Biggl[\varepsilon^{\overline{\overline{s}}}\mathbf{q}^{\overline{\overline{s}}}+\varepsilon^{\overline{\overline{s}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{s}}}\\
&\qquad+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{s\overline{\alpha}}\Biggl(\mu^{\overline{is}}+K_E^{\overline{\overline{is}}}+\frac{\mathbf{u}^{\overline{\overline{is}}}\cdot\mathbf{u}^{\overline{\overline{is}}}}{2}\Biggr)\mathbf{u}^{\overline{\overline{is}}}\\
&\qquad\qquad-\Biggl\langle\Biggl(\mathbf{t}_s-\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{j_s}\mathbf{I}\Biggr)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\Biggr\rangle_{\Omega_s,\Omega}\Biggr]\Biggr\}\\
&+\frac{1}{\theta^{\overline{\overline{w}}}}\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}}+\varepsilon^{\overline{\overline{w}}}p^{w}\mathbf{I}\right){:}\mathbf{d}^{\overline{\overline{w}}}+\frac{1}{\theta^{\overline{\overline{s}}}}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right){:}\mathbf{d}^{\overline{\overline{s}}}\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}}-\varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\mathbf{I}+\left\langle\left(\mathbf{I}-\mathbf{I}'_{ws}\right)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}\right]{:}\mathbf{d}^{\overline{\overline{ws}}}\\
&-\sum_{\alpha\in\mathfrak{I}_{/S}}\Biggl[\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}}\\
&\qquad+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\Biggl(\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\Biggr)\mathbf{u}^{\overline{\overline{i\alpha}}}\Biggr]\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)\\
&-\Biggl[\varepsilon^{\overline{\overline{s}}}\mathbf{q}^{\overline{\overline{s}}}+\varepsilon^{\overline{\overline{s}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{s}}}+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}}\Biggl(\mu^{\overline{is}}+K_E^{\overline{\overline{is}}}+\frac{\mathbf{u}^{\overline{\overline{is}}}\cdot\mathbf{u}^{\overline{\overline{is}}}}{2}\Biggr)\mathbf{u}^{\overline{\overline{is}}}
\end{aligned}
$$

$$- \left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s : \mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s, \Omega} \Bigg] \cdot \nabla \left(\frac{1}{\theta^{\overline{\overline{s}}}} \right)$$

$$- \sum_{\alpha \in \mathfrak{J}} \sum_{i \in \mathfrak{J}_{s/N}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \nabla \left[\mu^{\overline{i\alpha}} + K_E^{\overline{\overline{i\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \mathbf{u}^{\overline{\overline{i\alpha}}}}{2} + \psi^{\overline{i\alpha}} \right.$$

$$\left. - \left(\mu^{\overline{N\alpha}} + K_E^{\overline{\overline{N\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{N\alpha}}} \cdot \mathbf{u}^{\overline{\overline{N\alpha}}}}{2} + \psi^{\overline{N\alpha}} \right) \right]$$

$$- \sum_{\alpha \in \mathfrak{J}} \sum_{i \in \mathfrak{J}_s} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left(\mu^{\overline{i\alpha}} + K_E^{\overline{\overline{i\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \mathbf{u}^{\overline{\overline{i\alpha}}}}{2} + \psi^{\overline{i\alpha}} \right) \varepsilon^{\overline{\overline{i\alpha}}} r^{i\alpha}$$

$$+ \sum_{\alpha \in \mathfrak{J}} \sum_{i \in \mathfrak{J}_s} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \langle r_{i\alpha} \psi_{i\alpha} \rangle_{\Omega_\alpha, \Omega}$$

$$+ \sum_{i \in \mathfrak{J}_s} \overset{iw \to iws}{M} \left[\frac{1}{\theta^{\overline{\overline{w}}}} \left(\mu^{\overline{iw}} + K_E^{\overline{\overline{iw}}} + \frac{\mathbf{u}^{\overline{\overline{iw}}} \cdot \mathbf{u}^{\overline{\overline{iw}}}}{2} + \psi^{\overline{iw}} \right) \right.$$

$$\left. - \frac{1}{\theta^{\overline{\overline{ws}}}} \left(\mu^{\overline{iws}} + K_E^{\overline{\overline{iws}}} + \frac{\mathbf{u}^{\overline{\overline{iws}}} \cdot \mathbf{u}^{\overline{\overline{iws}}}}{2} + \psi^{\overline{iws}} \right) \right]$$

$$+ \sum_{i \in \mathfrak{J}_s} \overset{is \to iws}{M} \left[\frac{1}{\theta^{\overline{\overline{s}}}} \left(\mu^{\overline{is}} + K_E^{\overline{\overline{is}}} + \frac{\mathbf{u}^{\overline{\overline{is}}} \cdot \mathbf{u}^{\overline{\overline{is}}}}{2} + \psi^{\overline{is}} + \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}} : \mathbf{C}^s}{3 \rho^s j^s} \right) \right.$$

$$\left. - \frac{1}{\theta^{\overline{\overline{ws}}}} \left(\mu^{\overline{iws}} + K_E^{\overline{\overline{iws}}} + \frac{\mathbf{u}^{\overline{\overline{iws}}} \cdot \mathbf{u}^{\overline{\overline{iws}}}}{2} + \psi^{\overline{iws}} \right) \right]$$

$$+ \frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \left(\frac{\boldsymbol{\sigma}_s : \mathbf{C}_s}{\rho_s j_s} - \frac{\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s}{\rho_s} - \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}} : \mathbf{C}^s}{3 \rho^s j^s} \right) \rho_s \left(\mathbf{v}_s - \mathbf{v}_{ws} \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_{ws}, \Omega}$$

$$- \left\{ \overset{w \to ws}{Q_1} + \overset{w \to ws}{G_0} + \sum_{i \in \mathfrak{J}_s} \left(\overline{E}_{iw}^{\overline{ws}} + K_{Eiw}^{\overline{\overline{ws}}} + \frac{\mathbf{u}_{iw}^{\overline{\overline{ws}}} \cdot \mathbf{u}_{iw}^{\overline{\overline{ws}}}}{2} + \psi_{iw}^{\overline{ws}} \right) \overset{iw \to iws}{M} \right.$$

$$+ \left[\overset{w \to ws}{\mathbf{T}_0} + \sum_{i \in \mathfrak{J}_s} \left(\frac{\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} + \mathbf{u}_{iw}^{\overline{\overline{ws}}} \right) \overset{iw \to iws}{M} \right] \cdot \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)$$

$$\left. - \left\langle \mathbf{n}_w \cdot (\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}) p_w \right\rangle_{\Omega_{ws}, \Omega} \right\} \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right)$$

$$- \left\{ \overset{s \to ws}{Q_1} + \overset{s \to ws}{G_0} + \sum_{i \in \mathfrak{J}_s} \left(\overline{E}_{is}^{\overline{ws}} + K_{Eis}^{\overline{\overline{ws}}} + \frac{\mathbf{u}_{is}^{\overline{\overline{ws}}} \cdot \mathbf{u}_{is}^{\overline{\overline{ws}}}}{2} + \psi_{is}^{\overline{ws}} \right) \overset{is \to iws}{M} \right.$$

$$+ \left[\overset{s \to ws}{\mathbf{T}_0} + \sum_{i \in \mathfrak{J}_s} \left(\frac{\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} + \mathbf{u}_{is}^{\overline{\overline{ws}}} \right) \overset{is \to iws}{M} \right] \cdot \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)$$

$$\left. + \left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s \cdot (\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws}, \Omega} \right\} \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right)$$

$$-\frac{1}{\theta^{\overline{\overline{w}}}}\left\{\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}}-\nabla\left(\varepsilon^{\overline{\overline{w}}}p^{w}\right)\right. \tag*{32}$$

$$+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\left[\nabla\left(\mu^{\overline{iw}}+K_E^{\overline{\overline{iw}}}+\frac{\mathbf{u}^{\overline{\overline{iw}}}\cdot\mathbf{u}^{\overline{\overline{iw}}}}{2}+\psi^{\overline{iw}}\right)+\mathbf{g}^{\overline{iw}}\right] \tag*{33}$$

$$-\left[\overset{w\to ws}{\mathbf{T}_0}-\sum_{i\in\mathfrak{I}_s}\frac{\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{iw\to iws}{M}\right. \tag*{34}$$

$$\left.\left.+\sum_{i\in\mathfrak{I}_s}\left(\mathbf{v}_w^{\overline{ws}}+\mathbf{u}_{iw}^{\overline{\overline{ws}}}-\mathbf{v}^{\overline{s}}\right)\overset{iw\to iws}{M}\right]\right\}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right) \tag*{35}$$

$$-\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left\{\eta^{\overline{\overline{ws}}}\nabla\theta^{\overline{\overline{ws}}}+\nabla\cdot\left\langle\mathsf{I}'_{ws}\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}\right. \tag*{36}$$

$$+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\left[\nabla\left(\mu^{\overline{iws}}+K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\mathbf{u}^{\overline{\overline{iws}}}}{2}+\psi^{\overline{iws}}\right)+\mathbf{g}^{\overline{iws}}\right] \tag*{37}$$

$$+\overset{w\to ws}{\mathbf{T}_0}-\sum_{i\in\mathfrak{I}_s}\frac{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{iw\to iws}{M}+\sum_{i\in\mathfrak{I}_s}\left(\mathbf{v}_w^{\overline{ws}}+\mathbf{u}_{iw}^{\overline{\overline{ws}}}-\mathbf{v}^{\overline{s}}\right)\overset{iw\to iws}{M} \tag*{38}$$

$$+\overset{s\to ws}{\mathbf{T}_0}-\sum_{i\in\mathfrak{I}_s}\frac{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{is\to iws}{M}+\sum_{i\in\mathfrak{I}_s}\left(\mathbf{v}_s^{\overline{ws}}+\mathbf{u}_{is}^{\overline{\overline{ws}}}-\mathbf{v}^{\overline{s}}\right)\overset{is\to iws}{M} \tag*{39}$$

$$-\left\langle\eta_{ws}\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\theta^{\overline{\overline{ws}}} \tag*{40}$$

$$-\sum_{i\in\mathfrak{I}_s}\left\langle\rho_{ws}\omega_{iws}\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\left(\mu^{\overline{iws}}+K_E^{\overline{\overline{iws}}}\right. \tag*{41}$$

$$\left.\left.+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}+\psi^{\overline{iws}}\right)\right\}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right) \tag*{42}$$

$$+\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left\langle\left[p_w\mathbf{n}_w-\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s+\gamma_{ws}\left(\nabla'\cdot\mathsf{I}'_{ws}\right)\right.\right. \tag*{43}$$

$$\left.\left.+\sum_{i\in\mathfrak{I}_s}\rho_{ws}\omega_{iws}\mathbf{g}_{iws}\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right]\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} \tag*{44}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathsf{I}'_{ws}\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} \tag*{45}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\cdot\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s:\frac{\mathsf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega} \tag*{46}$$

$$+\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left\langle\eta_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\theta^{\overline{\overline{ws}}} \tag*{47}$$

$$+\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\nabla\cdot\left\langle\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}}\right)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega} \tag*{48}$$

$$
\begin{aligned}
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\sum_{i\in\mathfrak{I}_s}\left\langle\rho_{ws}\omega_{iws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}}\right)\cdot\left(\mathbf{l}-\mathbf{l}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\left(\mu^{\overline{iws}}+\right. && 49\\
&\qquad\left. K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}+\psi^{\overline{iws}}\right) && 50\\
&=\sum_{\alpha\in\mathfrak{I}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. && 51
\end{aligned}
\tag{10.14}
$$

Note that in line 18 of this equation, the superscript "*N*" refers to one of the chemical species in the system chosen to be the reference species.

The CEI given by Eq. (10.14) is an archival equation that can serve as a basis for the derivation of a hierarchy of closed models of varying sophistication. Accomplishing this objective requires reducing the CEI to the strict force-flux form provided by the simplified entropy inequality, SEI. An example SEI is derived in the following section. Although the CEI is built only on the primary restrictions, approximations must be integrated into this equation to develop SEI forms. These assumptions must be reconsidered if it is learned that a resultant model is not consistent with a physical system that is intended to be modeled.

10.4 Simplified Entropy Inequality

This section is concerned with the reduction of Eq. (10.14) to an SEI that is of assistance in guiding the formulation of closure relations for the conservation equations. This reduction requires SEI approximations and may include secondary restrictions. The distinction between these two classes of stipulations is that SEI approximations involve mathematical restatements of groupings of terms, and secondary restrictions limit the generality of the formulation by reducing the entities or phenomena being modeled. Since alternative approximations may be made to reduce the CEI to an SEI, the SEI is not a unique inequality. The manipulations needed to derive an SEI from a CEI are less than those needed in deriving the CEI. For this reason, use of Eq. (10.14) as a starting point for examination of various approximations is convenient. A hierarchy of TCAT models can also be derived based on a particular form of an SEI. Thus, the SEI is also a convenient starting point. The approach to obtaining the SEI from the CEI for this problem parallels that employed in Sect. 9.5. Emphasis here is on the additional considerations required due to the incorporation of explicit modeling of chemical species.

10.4.1 Elimination of Small Terms

One of the assets of Table 10.2 is that it can be used to identify quickly terms in Eq. (10.14) that require additional study to obtain an SEI. These terms are the ones in the lines that do not have a macroscale force listed. Rather than being in macroscale force-flux product form, they are collections of terms that either need to be eliminated or otherwise approximated macroscopically and integrated into the force-flux formalism. Reasonable assumptions must be found that facilitate these changes. In this section, we will formally state the rationale in SEI approximations for eliminating some groups of terms that are typically small.

Lines 1–10 in Eq. (10.14) are not in force-flux form. However, lines 1–5 provide groupings that are the difference between the entropy source and the energy source divided by the temperature for each entity. Lines 6–10 involve the differences between non-advective energy fluxes and entropy fluxes. We propose that these pairs of differences are negligible such that the following SEI approximation is reasonable:

SEI Approximation 10.1 (Macroscopically Simple System)
The system of concern is macroscopically simple, such that the entropy source is balanced by the sum of a heat source and deviation terms such that

$$\begin{aligned}
&\epsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left[\epsilon^{\overline{\overline{\alpha}}} h^{\alpha} + \left\langle \eta_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \right. \\
&\quad \left. + \sum_{i \in \mathfrak{J}_s} \left\langle \rho_{\alpha} \omega_{i\alpha} \frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t} \left(\mu_{i\alpha} + \psi_{i\alpha} - \mu^{\overline{i\alpha}} - K_E^{\overline{\overline{i\alpha}}} - \frac{\mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \mathbf{u}^{\overline{\overline{i\alpha}}}}{2} - \psi^{\overline{i\alpha}} \right) \right\rangle_{\Omega_{\alpha},\Omega} \right] = 0 \\
&\qquad \textit{for } \alpha \in \mathfrak{J}_{\mathrm{P}}
\end{aligned} \tag{10.15}$$

and

$$\begin{aligned}
&\epsilon^{\overline{\overline{ws}}} b^{ws} - \frac{1}{\theta^{\overline{\overline{ws}}}} \left[\epsilon^{\overline{\overline{ws}}} h^{ws} + \left\langle \eta_{ws} \frac{\mathrm{D}'^{\overline{s}} \left(\theta_{ws} - \theta^{\overline{\overline{ws}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{ws},\Omega} \right. \\
&\quad + \sum_{i \in \mathfrak{J}_s} \left\langle \rho_{ws} \omega_{iws} \frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t} \left(\mu_{iws} + \psi_{iws} - \mu^{\overline{iws}} \right. \right. \\
&\qquad \left. \left. \left. - K_E^{\overline{\overline{iws}}} - \frac{\mathbf{u}^{\overline{\overline{iws}}} \cdot \mathbf{u}^{\overline{\overline{iws}}}}{2} - \psi^{\overline{iws}} \right) \right\rangle_{\Omega_{ws},\Omega} \right] = 0\,;
\end{aligned} \tag{10.16}$$

and the entropy flux is balanced by a non-advective energy flux for all entities, consisting of heat and mechanical contributions, such that

$$\epsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}} - \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\epsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}} + \epsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}} + \sum_{i\in\mathfrak{I}_s} \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\mu^{\overline{i\alpha}} + K_E^{\overline{\overline{i\alpha}}} + \frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\mathbf{u}^{\overline{\overline{i\alpha}}}\right] = \mathbf{0}$$

$$\text{for } \alpha \in \{w, ws\} \qquad (10.17)$$

and

$$\epsilon^{\overline{\overline{s}}}\boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{s}}}}\left[\epsilon^{\overline{\overline{s}}}\mathbf{q}^{\overline{\overline{s}}} + \epsilon^{\overline{\overline{s}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{s}}} + \sum_{i\in\mathfrak{I}_s} \epsilon^{\overline{\overline{s}}}\rho^{s}\omega^{s\overline{\alpha}}\left(\mu^{\overline{is}} + K_E^{\overline{\overline{is}}} + \frac{\mathbf{u}^{\overline{\overline{is}}}\cdot\mathbf{u}^{\overline{\overline{is}}}}{2}\right)\mathbf{u}^{\overline{\overline{is}}}\right.$$

$$\left. - \left\langle \left(\mathsf{t}_s - \frac{\boldsymbol{\sigma}_s:\mathsf{C}_s}{\dot{j}_s}\mathsf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right] = \mathbf{0}\,. \qquad (10.18)$$

Based on SEI Approximation 10.1, the first 10 lines in Eq. (10.14) may be dropped. This approximation is reasonable because like terms have been paired—entropy and heat sources and entropy and heat fluxes. Terms involving dispersion and deviations between macroscale and microscale quantities are subscale processes in the formulation and contribute as apparent energy sources and fluxes. The averages of material derivative terms of differences between microscale and macroscale quantities in Eqs. (10.15) and (10.16) are subscale energy sources that arise due to the averaging of the thermodynamics.

Lines 45–46 in Eq. (10.14) each involve the average of a quantity that is zero at equilibrium (see Eqs. (4.54) and (4.106)) and a difference between the microscale and macroscale solid-phase velocity. For the system being considered, where the solid-phase velocity is small enough that this velocity difference can be considered negligible, these two lines of the CEI can be neglected. This is stated in an SEI approximation:

SEI Approximation 10.2 (Solid-phase Velocity)
Expressions that involve the average of a product of the difference between the microscale and macroscale solid-phase velocities and another term known to vanish at equilibrium are assumed to be negligible.

This SEI approximation was employed in the last chapter in the absence of species transport modeling. It is a reasonable approximation for many, if not most, porous medium problems, with solid phase velocities much smaller than fluid phase velocities. Note that because of this assumption, the averaging operator term in Line 16 of Eq. (10.14), which involves a product of the solid-phase velocity difference and the temperature gradient, is also considered to be negligible.

Lines 47–50 involve the average of the difference between the normal component of the microscale *ws* velocity and the average normal component. Because the interface moves slowly, this difference in velocities is small. For this reason, the sum of terms in lines 47–50 is neglected relative to other terms in the CEI. This is stated formally in the following SEI approximation:

SEI Approximation 10.3 (Interface Velocity Difference)
Expressions involving the average of the difference between the microscale normal

flow velocity in a fluid-solid interface and the average normal flow of the macroscale velocity in a fluid-solid interface are negligible.

An additional SEI approximation is introduced to allow the elimination of a term involving mass exchange between the solid and the interface, specifically the grouping in line 25 of Eq. (10.14). This term is negligible when the correlation between the stress differences and the mass exchange is small or if the mass exchange at the surface is negligible. In any event, this term is small compared to the mass exchange term of lines 23 and 24. Thus we make the approximation as follows:

SEI Approximation 10.4 (Stress Difference and Mass Exchange)
Terms that involve a product of the microscale mass exchange between the solid phase and the ws interface and the difference between the microscale and macroscale normal solid stress at the interface can be neglected.

10.4.2 Breaking of Averages

As was done in the last chapter, we will break averages of some products of microscale quantities. The essential feature of the approximations is that the average of a product of terms is set to be essentially equal to the product of the averages of the quantities considered. In general, such an approximation is strictly correct only if the microscale factors are uncorrelated. Here we will assume that the correlation is negligible or that the quantities themselves are so small that the error introduced by neglecting the correlation is negligible. Assumptions of this type may be applied only with caution and only for particular physical variables. Thus, it is important that the use of these approximations be clearly identified as they provide fertile ground for investigation of alternative approximations. For the most part, the SEI approximations to be applied here are the same as those introduced previously in Sect. 9.5.3. Thus, the rationale behind each of the approximations will be abbreviated.

The orientation of the interface between the phases will be considered to be uncorrelated to any physical properties. This allows the breaking of the products as follows:

SEI Approximation 10.5 (Geometric Orientation Products)
The average over the ws interface of a product of the microscale geometric orientation tensor $\mathsf{G}_{ws} = \mathsf{I} - \mathsf{I}'_{ws}$ with a microscale scalar f_α can be evaluated as the product of the macroscale averages of the two components of the original expression such that

$$\langle \mathsf{G}_{ws} f_\alpha \rangle_{\Omega_{ws},\Omega} = \varepsilon^{\overline{\overline{ws}}} \mathsf{G}^{ws} f_\alpha^{ws} \quad \textit{for } \alpha \in \mathfrak{J}_{\mathrm{P}} \tag{10.19}$$

and

$$\langle \mathsf{G}_{ws} f_{ws} \rangle_{\Omega_{ws},\Omega} = \varepsilon^{\overline{\overline{ws}}} \mathsf{G}^{ws} f^{ws} \ . \tag{10.20}$$

This approximation is used to evaluate terms appearing in lines 12, 36, 40, and 41 of Eq. (10.14).

The equation relating the evolution of the solid-phase volume fraction to the movement of the *ws* interface was derived as Eq. (8.6) with

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} = \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} . \tag{10.21}$$

The quantity within the averaging operator on the right side appears in CEI Eq. (10.14) multiplied by a microscale quantity in lines 28[3], 31, and 43–44. This product is broken making use of the following approximation:

SEI Approximation 10.6 (Evolution Product)
The average over the ws interface of a term involving the product of $\mathbf{n}_s \cdot (\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}})$ *with a microscale scalar can be approximated as the product of the macroscale averages of the two factors. In conjunction with Eq. (10.21), this approximation yields*

$$\left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right) f_\alpha \right\rangle_{\Omega_{ws},\Omega} = \frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} f_\alpha^{ws} \quad \text{for } \alpha \in \{w, s\} \tag{10.22}$$

and

$$\left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right) f_{ws} \right\rangle_{\Omega_{ws},\Omega} = \frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} f^{ws} . \tag{10.23}$$

An additional SEI approximation is introduced to facilitate breaking of the product involving $\nabla'\cdot\mathbf{l}'_{ws} = -\mathbf{n}_s \nabla'\cdot\mathbf{n}_s$ in line 43 of Eq. (10.14). Application of SEI Approximation 10.6 still leaves the product of microscale interfacial tension and curvature to be evaluated. This is accomplished as follows:

SEI Approximation 10.7 (Product of Curvature and Tension)
The average over the ws interface of a term involving the product of the microscale curvature $\nabla'\cdot\mathbf{n}_s$ *with the microscale interfacial tension* γ_{ws} *can be approximated as the product of the macroscale averages of the two factors such that*

$$\left\langle \gamma_{ws} \left(\nabla'\cdot\mathbf{n}_s\right)\right\rangle_{\Omega_{ws},\Omega_{ws}} = \langle \gamma_{ws} \rangle_{\Omega_{ws},\Omega_{ws}} \left\langle \nabla'\cdot\mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega_{ws}} = \gamma^{ws} J_s^{ws} , \tag{10.24}$$

where $J_s^{ws} = \langle \nabla'\cdot\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}}$ *is the average curvature of the ws interface.*

SEI Approximations 10.6 and 10.7 are employed together in lines 43 and 44 to obtain

$$\left\langle \gamma_{ws} \left(\nabla'\cdot\mathbf{l}'_{ws}\right) \cdot \left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} = -\gamma^{ws} J_s^{ws} \frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} . \tag{10.25}$$

---

[3] In line 28, the unit vector is $\mathbf{n}_w$ rather than $\mathbf{n}_s$, but since $\mathbf{n}_w = -\mathbf{n}_s$ on the interface, the presence of $\mathbf{n}_w$ simply introduces a minus sign on the right side of the equation.

10.4.3 General SEI

Use of SEI Approximations 10.1 through 10.7 in the CEI of Eq. (10.14) followed by minor collection of terms yields the general SEI,

$$
\begin{aligned}
&\frac{1}{\theta^{\overline{\overline{\overline{w}}}}}\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}}+\varepsilon^{\overline{\overline{w}}}p^{w}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{w}}}+\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}} && 1\\
&+\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}}-\varepsilon^{\overline{\overline{ws}}}(\mathbf{I}-\mathbf{G}^{ws})\gamma^{ws}\right]:\mathbf{d}^{\overline{\overline{ws}}} && 2\\
&-\sum_{\alpha\in\mathfrak{J}}\left[\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}}\right. && 3\\
&\qquad\left.+\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{\overline{i\alpha}}}}\cdot\mathbf{u}^{\overline{\overline{\overline{i\alpha}}}}}{2}\right)\mathbf{u}^{\overline{\overline{i\alpha}}}\right]\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\right) && 4\\
&-\sum_{\alpha\in\mathfrak{J}}\sum_{i\in\mathfrak{J}_{s/N}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\nabla\left[\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{\overline{i\alpha}}}}\cdot\mathbf{u}^{\overline{\overline{\overline{i\alpha}}}}}{2}+\psi^{\overline{i\alpha}}\right. && 5\\
&\qquad\left.-\left(\mu^{\overline{N\alpha}}+K_E^{\overline{\overline{N\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{\overline{N\alpha}}}}\cdot\mathbf{u}^{\overline{\overline{\overline{N\alpha}}}}}{2}+\psi^{\overline{N\alpha}}\right)\right] && 6\\
&-\sum_{\alpha\in\mathfrak{J}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left(\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{\overline{i\alpha}}}}\cdot\mathbf{u}^{\overline{\overline{\overline{i\alpha}}}}}{2}+\psi^{\overline{i\alpha}}\right)\varepsilon^{\overline{\overline{i\alpha}}}r^{i\alpha} && 7\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\langle r_{i\alpha}\psi_{i\alpha}\rangle_{\Omega_\alpha,\Omega} && 8\\
&+\sum_{i\in\mathfrak{J}_s}\overset{iw\to iws}{M}\left[\frac{1}{\theta^{\overline{\overline{\overline{w}}}}}\left(\mu^{\overline{iw}}+K_E^{\overline{\overline{iw}}}+\frac{\mathbf{u}^{\overline{\overline{\overline{iw}}}}\cdot\mathbf{u}^{\overline{\overline{\overline{iw}}}}}{2}+\psi^{\overline{iw}}\right)\right. && 9\\
&\qquad\left.-\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left(\mu^{\overline{iws}}+K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{\overline{iws}}}}\cdot\mathbf{u}^{\overline{\overline{\overline{iws}}}}}{2}+\psi^{\overline{iws}}\right)\right] && 10\\
&+\sum_{i\in\mathfrak{J}_s}\overset{is\to iws}{M}\left[\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left(\mu^{\overline{is}}+K_E^{\overline{\overline{is}}}+\frac{\mathbf{u}^{\overline{\overline{\overline{is}}}}\cdot\mathbf{u}^{\overline{\overline{\overline{is}}}}}{2}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{is}}\right)\right. && 11\\
&\qquad\left.-\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left(\mu^{\overline{iws}}+K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{\overline{iws}}}}\cdot\mathbf{u}^{\overline{\overline{\overline{iws}}}}}{2}+\psi^{\overline{iws}}\right)\right] && 12\\
&-\left\{\overset{w\to ws}{Q_1}+\overset{w\to ws}{G_0}+\sum_{i\in\mathfrak{J}_s}\left(\overline{E}_{iw}^{\overline{ws}}+K_{Eiw}^{\overline{\overline{ws}}}+\frac{\mathbf{u}_{iw}^{\overline{\overline{\overline{ws}}}}\cdot\mathbf{u}_{iw}^{\overline{\overline{\overline{ws}}}}}{2}+\psi_{iw}^{\overline{ws}}\right)\overset{iw\to iws}{M}\right. && 13\\
&\qquad\left.+\left[\overset{w\to ws}{\mathbf{T}_0}+\sum_{i\in\mathfrak{J}_s}\left(\frac{\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}}{2}+\mathbf{u}_{iw}^{\overline{\overline{ws}}}\right)\overset{iw\to iws}{M}\right]\cdot\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)\right. && 14
\end{aligned}
$$

$$+ p_w^{ws} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} \Bigg\} \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right)$$

$$- \Bigg\{ \overset{s\rightarrow ws}{Q_1} + \overset{s\rightarrow ws}{G_0} + \sum_{i\in\mathfrak{J}_s} \left(\overline{E}_{is}^{\overline{ws}} + K_{Eis}^{\overline{\overline{ws}}} + \frac{\mathbf{u}_{is}^{\overline{\overline{ws}}}\cdot\mathbf{u}_{is}^{\overline{\overline{ws}}}}{2} + \psi_{is}^{\overline{ws}} \right) \overset{is\rightarrow iws}{M}$$

$$+ \left[\overset{s\rightarrow ws}{\mathbf{T}_0} + \sum_{i\in\mathfrak{J}_s} \left(\frac{\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} + \mathbf{u}_{is}^{\overline{\overline{ws}}} \right) \overset{is\rightarrow iws}{M} \right] \cdot \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)$$

$$+ \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} \Bigg\} \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right)$$

$$- \frac{1}{\theta^{\overline{\overline{w}}}} \Bigg\{ \eta^{\overline{\overline{w}}} \nabla \theta^{\overline{\overline{w}}} - \nabla \left(\varepsilon^{\overline{\overline{w}}} p^w \right)$$

$$+ \sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{w}}} \rho^w \omega^{i\overline{w}} \left[\nabla \left(\mu^{\overline{iw}} + K_E^{\overline{\overline{iw}}} + \frac{\mathbf{u}^{\overline{\overline{iw}}}\cdot\mathbf{u}^{\overline{\overline{iw}}}}{2} + \psi^{\overline{iw}} \right) + \mathbf{g}^{\overline{iw}} \right]$$

$$- \Bigg[\overset{w\rightarrow ws}{\mathbf{T}_0} - \sum_{i\in\mathfrak{J}_s} \frac{\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}} \right)}{2} \overset{iw\rightarrow iws}{M}$$

$$+ \sum_{i\in\mathfrak{J}_s} \left(\mathbf{v}_w^{\overline{ws}} + \mathbf{u}_{iw}^{\overline{\overline{ws}}} - \mathbf{v}^{\overline{s}} \right) \overset{iw\rightarrow iws}{M} \Bigg] \Bigg\} \cdot \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}} \right)$$

$$- \frac{1}{\theta^{\overline{\overline{ws}}}} \Bigg\{ \eta^{\overline{\overline{ws}}} \left(\mathsf{I} - \mathsf{G}^{ws} \right) \cdot \nabla \theta^{\overline{\overline{ws}}} + \nabla\cdot \left[\varepsilon^{\overline{\overline{ws}}} \left(\mathsf{I} - \mathsf{G}^{ws} \right) \gamma^{ws} \right]$$

$$+ \sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{ws}}} \rho^{ws} \omega^{i\overline{ws}} \left(\mathsf{I} - \mathsf{G}^{ws} \right) \cdot \nabla \left(\mu^{\overline{iws}} + K_E^{\overline{\overline{iws}}} + \frac{\mathbf{u}^{\overline{\overline{iws}}}\mathbf{u}^{\overline{\overline{iws}}}}{2} + \psi^{\overline{iws}} \right)$$

$$+ \sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{ws}}} \rho^{ws} \omega^{i\overline{ws}} \mathbf{g}^{\overline{iws}}$$

$$+ \overset{w\rightarrow ws}{\mathbf{T}_0} - \sum_{i\in\mathfrak{J}_s} \frac{\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)}{2} \overset{iw\rightarrow iws}{M} + \sum_{i\in\mathfrak{J}_s} \left(\mathbf{v}_w^{\overline{ws}} + \mathbf{u}_{iw}^{\overline{\overline{ws}}} - \mathbf{v}^{\overline{s}} \right) \overset{iw\rightarrow iws}{M}$$

$$+ \overset{s\rightarrow ws}{\mathbf{T}_0} - \sum_{i\in\mathfrak{J}_s} \frac{\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)}{2} \overset{is\rightarrow iws}{M}$$

$$+ \sum_{i\in\mathfrak{J}_s} \left(\mathbf{v}_s^{\overline{ws}} + \mathbf{u}_{is}^{\overline{\overline{ws}}} - \mathbf{v}^{\overline{s}} \right) \overset{is\rightarrow iws}{M} \Bigg\} \cdot \left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)$$

$$- \frac{1}{\theta^{\overline{\overline{ws}}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} \Bigg(p_w^{ws} + \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}} + \gamma^{ws} J_s^{ws}$$

$$- \sum_{i\in\mathfrak{J}_s} \langle \rho_{ws} \omega_{iws} \mathbf{g}_{iws} \cdot \mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}} \Bigg)$$

$$= \sum_{\alpha\in\mathfrak{J}} \Lambda^{\overline{\overline{\alpha}}} \geq 0 \,. \qquad 31$$

$$\tag{10.26}$$

With fewer approximations applied to the CEI, this SEI would be more general. However, the SEI approximations imposed here are minimal in most cases and thus, for our purposes, Eq. (10.26) will be referred to as the "general" SEI. All the terms in this equation are in force-flux form except the chemical reaction expressions in lines 7 and 8. This shortcoming is dealt with, depending on the system, as will be demonstrated subsequently. For now, we will comment that the usual approach is to neglect the species dependence of $\psi_{i\alpha}$, which eliminates line 8, and to handle the reaction term using a macroscale affinity, similarly to Eq. (5.38) in the development of a microscale model. In addition to the forces listed in Table 10.2, the quantity in parentheses in lines 29 and 30 emerges as another force. This force was shown to be zero at equilibrium in the derivation of Eq. (7.115).

Under the umbrella provided by the general SEI, we can apply some restrictions consistent with a system of interest. The primary goal here is to demonstrate how species modeling extends the analysis of the last chapter in which only entities were considered. We will analyze a system that represents an extension of the last chapter by including species transport for a non-isothermal system.

10.5 SEI for Application to Non-isothermal Species Transport

As was demonstrated in Sect. 9.6, application of the SEI to determine closure relations involves:

1. using secondary restrictions that simplify the problem by eliminating processes from further study that are not of interest;
2. counting the number of variables in contrast to the number of equations so that the deficiency in variables that must be addressed is determined;
3. reducing the deficiency in equations by use of state equations and approximate relations between variables; and
4. eliminating the remaining deficiency in the number of equations using closure relations.

These steps will be followed here, in brief, with emphasis on the last item.

10.5.1 Imposition of Secondary Restrictions

Based on the belief that working with a simpler form of the general SEI of Eq. (10.26) to obtain closure relations will be more illuminating, we will apply secondary restrictions that provide for simplification but do not exclude a wide range of interesting systems. The first simplification relates to the body force and its potential:

Secondary Restriction 10.1 (Body Force Potential)
The macroscale species body force vector for a species in an entity, $\mathbf{g}^{\overline{i\alpha}}$*, and the average of body force potential,* $\psi^{\overline{i\alpha}}$*, will be considered to be independent of chemical species such that*

$$\mathbf{g}^{\overline{i\alpha}} = \mathbf{g}^{\overline{\alpha}} \quad \textit{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J} \tag{10.27}$$

and

$$\psi^{\overline{i\alpha}} = \psi^{\overline{\alpha}} \quad \textit{for } i \in \mathfrak{J}_s, \alpha \in \mathfrak{J}\,. \tag{10.28}$$

When $\mathbf{g}^{\overline{\alpha}}$ is taken to be a constant gravitational acceleration, it is independent of the entity. In this instance, the microscale potential function is also independent of entity, but its average is not necessarily independent of either the species or the entity. When the concentration or density is variable and/or the phase distribution is not uniform in an averaging volume, dependence of $\psi^{\overline{i\alpha}}$ on the chemical species and entity can arise. Typically, this effect is small. When the body force includes other effects, such as an electrical effect, Secondary Restriction 10.1 will not apply. However, as stated, this restriction causes line 8 of Eq. (10.26) and the product $\psi^{\overline{i\alpha}} r^{i\alpha}$ in line 7 to drop out because the sum of the production rates of species over all species within a phase must be zero.

Another restriction that is imposed here is that the flows are slow enough that the deviation kinetic energy and the inner product of the dispersion velocity with itself are negligibly small. This condition may be stated as:

Secondary Restriction 10.2 (Deviation Velocities Squared)
The deviation velocities that enter into the analysis, $\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha}$*,* $\mathbf{v}_{\alpha} - \mathbf{v}^{\overline{\alpha}}$*, and* $\mathbf{u}^{\overline{\overline{i\alpha}}}$ *for* $\alpha \in \mathfrak{J}$*, are restricted to be small enough that their magnitude squared may be neglected in the analysis. In the macroscale equations,* $K_E^{\overline{\overline{i\alpha}}}$*,* $\mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \mathbf{u}^{\overline{\overline{i\alpha}}}$*, and the products of mass exchange terms with the magnitude of these velocity differences may be eliminated.*

We will consider systems where the mass per area of the interface is zero. Thus the interface is massless, and any mass transferred from one phase to the interface is immediately transferred into the adjacent phase. The restriction on interfacial mass density be stated as a secondary restriction:

Secondary Restriction 10.3 (Massless Interface)
No mass exists or accumulates in the ws interface such that $\rho^{ws} = 0$*.*

When this restriction applies, physical reasoning suggests, and mass conservation described by Eq. (10.3) confirms, that the mass transferred from the w phase must equal the amount that enters the s phase. Thus, Secondary Restriction 10.3 requires

$$\overset{iw\to iws}{M} = -\overset{is\to iws}{M} = \overset{iw\to is}{M} = -\overset{is\to iw}{M} \quad \text{for } i \in \mathfrak{J}_s\,. \tag{10.29}$$

Additionally, because $\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{ws}}}$ as obtained from Eqs. (6.154) and (6.199) depends on the interface density, this restriction requires that $\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{ws}}} = 0$.

A last secondary restriction involves formulation of the chemical reaction in terms of chemical affinity. An analogous rearrangement was implemented in Sect. 5.4.3 when deriving the microscale CEI. Here, it falls with the simplification of the SEI because it depends on Secondary Restrictions 10.1 and 10.2 for implementation. We identify the formation of species i in entity α as

$$r^{i\alpha} = \sum_{k\in\mathfrak{I}_{\mathrm{rxn}\alpha}} \nu_{ik\alpha}\mathrm{MW}_i R^{k\alpha} \,, \tag{10.30}$$

where $\mathfrak{I}_{\mathrm{rxn}\alpha}$ is the set of N_{rxn} reactions that occur in entity α, $\nu_{ik\alpha}$ is the stoichiometric coefficient for component i in reaction k in entity α, MW_i is the molecular weight of species i and $R^{k\alpha}$ is the molecular rate of reaction k in entity α. The affinity of reaction k in entity α, denoted $A^{k\alpha}$, is a measure of disequilibrium of the reaction with

$$A^{k\alpha} = \sum_{i\in\mathfrak{I}_s} \mu^{\overline{i\alpha}}\nu_{ik\alpha}\mathrm{MW}_i \quad \text{for } k\in\mathfrak{I}_{\mathrm{rxn}\alpha}, \alpha\in\mathfrak{I} \,. \tag{10.31}$$

The affinity is typically invoked at the microscale [1] and is related to the change of Gibbs free energy with respect to the extent of completion of the reaction. We consider a similar relation to exist at the macroscale and observe that the affinity is zero at equilibrium. With these definitions we can pose the following:

Secondary Restriction 10.4 (Affinity of a Chemical Reaction)
The macroscale affinity of a chemical reaction is defined analogously to the microscopic affinity such that

$$\sum_{i\in\mathfrak{I}_s} \mu^{\overline{i\alpha}} r^{i\alpha} = \sum_{i\in\mathfrak{I}_s} \sum_{k\in\mathfrak{I}_{\mathrm{rxn}\alpha}} \mu^{\overline{i\alpha}}\nu_{ik\alpha}\mathrm{MW}_i R^{k\alpha} = \sum_{k\in\mathfrak{I}_{\mathrm{rxn}\alpha}} A^{k\alpha}R^{k\alpha} \quad \textit{for } \alpha\in\mathfrak{I} \,. \tag{10.32}$$

Implementation of Secondary Restrictions 10.1–10.4 in the general SEI of Eq. (10.26) provides the somewhat simpler SEI,

$$\begin{aligned}
&\frac{1}{\theta^{\overline{\overline{\overline{w}}}}}\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{w}}} p^{w}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{w}}} + \frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}} && 1\\
&+ \frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}} - \varepsilon^{\overline{\overline{ws}}}(\mathbf{I}-\mathbf{G}^{ws})\gamma^{ws}\right]:\mathbf{d}^{\overline{\overline{ws}}} && 2\\
&- \sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}} + \sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right)\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\right) && 3\\
&- \varepsilon^{\overline{\overline{ws}}}\mathbf{q}^{\overline{\overline{ws}}}\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\right) && 4\\
&- \sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\sum_{i\in\mathfrak{I}_{s/N}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\nabla\left(\mu^{\overline{i\alpha}} - \mu^{\overline{N\alpha}}\right) && 5
\end{aligned}$$

$$
\begin{aligned}
&-\sum_{\alpha\in\mathfrak{J}_{\mathrm{P}}}\;\sum_{k\in\mathfrak{J}_{\mathrm{rxn}\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}R^{k\alpha}A^{k\alpha} && 6\\
&+\sum_{i\in\mathfrak{J}_s}\overset{iw\to is}{M}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{iw}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{is}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{s}}\right)\right] && 7\\
&-\Bigg\{\overset{w\to ws}{Q_1}+\overset{w\to ws}{G_0}+\sum_{i\in\mathfrak{J}_s}\left(\overline{E}_{iw}^{\overline{ws}}+\psi_{w}^{\overline{ws}}\right)\overset{iw\to is}{M} && 8\\
&\qquad+\overset{w\to ws}{\mathbf{T}_0}\cdot\left(\mathbf{v}_{w}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)+p_{w}^{ws}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\Bigg\}\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right) && 9\\
&-\Bigg\{\overset{s\to ws}{Q_1}+\overset{s\to ws}{G_0}-\sum_{i\in\mathfrak{J}_s}\left(\overline{E}_{is}^{\overline{ws}}+\psi_{s}^{\overline{ws}}\right)\overset{iw\to is}{M} && 10\\
&\qquad+\overset{s\to ws}{\mathbf{T}_0}\cdot\left(\mathbf{v}_{s}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\Bigg\}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right) && 11\\
&-\frac{1}{\theta^{\overline{\overline{w}}}}\Bigg\{\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}}-\nabla\left(\varepsilon^{\overline{\overline{w}}}p^{w}\right)+\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\left[\nabla\left(\mu^{\overline{iw}}+\psi^{\overline{w}}\right)+\mathbf{g}^{\overline{w}}\right] && 12\\
&\qquad-\overset{w\to ws}{\mathbf{T}_0}\Bigg\}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right) && 13\\
&-\frac{1}{\theta^{\overline{\overline{ws}}}}\Bigg\{\eta^{\overline{\overline{ws}}}\left(\mathbf{I}-\mathbf{G}^{ws}\right)\cdot\nabla\theta^{\overline{\overline{ws}}}+\nabla\cdot\left[\varepsilon^{\overline{\overline{ws}}}\left(\mathbf{I}-\mathbf{G}^{ws}\right)\gamma^{ws}\right] && 14\\
&\qquad+\overset{w\to ws}{\mathbf{T}_0}+\overset{s\to ws}{\mathbf{T}_0}\Bigg\}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right) && 15\\
&-\frac{1}{\theta^{\overline{\overline{ws}}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\left(p_{w}^{ws}+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}+\gamma^{ws}J_{s}^{ws}\right) && 16\\
&=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. && 17
\end{aligned}
\tag{10.33}
$$

This equation is arranged so that all terms are products of independent macroscale forces and fluxes. The groupings of forces and fluxes are not unique. In each force-flux pair, the force is listed as the second factor in the product. The forces have all been shown to be zero at equilibrium. The fact that the fluxes must also be zero at equilibrium provides a constraint on their forms and will be used to develop approximate closure relations.

We will now demonstrate how this SEI for non-isothermal species transport can be employed to model four cases: isothermal transport of species with no interphase exchange of mass; isothermal transport with interphase exchange of mass; single-temperature, non-isothermal transport; and two-temperature, non-isothermal transport with interphase exchange of mass. The last of these four cases is the most general and reduces to the other cases with appropriate restrictions. However, it is worthwhile, for illustrative purposes at least, to set up the first three examples as special cases so that the conditions and approximations needed just for those cases are more easily identified.

10.6 Isothermal Transport with No Interphase Mass Exchange

This case considers transport and reaction of a chemical species within the phases. In the limit where there is only one species present, the resulting model should be identical to that of Chap. 9. We will consider the elements of this case here.

10.6.1 Simplification of SEI

For this isothermal case with no inter-entity mass exchange, an additional secondary restriction may be stated:

Secondary Restriction 10.5 (Isothermal, No Mass Exchange)
The system is constrained to be isothermal with no temperature gradients such that

$$\theta^{\overline{\overline{\alpha}}} = \theta^{\cdot} \quad \text{for } \alpha \in \mathfrak{I} \tag{10.34}$$

and

$$\nabla \theta^{\overline{\overline{\alpha}}} = 0 \quad \text{for } \alpha \in \mathfrak{I}\,; \tag{10.35}$$

additionally, no mass exchange occurs between the phases so that

$$\overset{iw\to is}{M} = 0 \quad \text{for } i \in \mathfrak{I}_s\,. \tag{10.36}$$

Application of these additional constraints to the SEI of Eq. (10.33) eliminates lines 3, 4, and 7–11 as well as the terms involving a temperature gradient in lines 12 and 14. After multiplication by the constant temperature, $\theta^{\cdot}$, the resulting equation is

$$\begin{aligned}
&\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{w}}} p^{w}\mathbf{I}\right) : \mathbf{d}^{\overline{\overline{w}}} + \left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right) : \mathbf{d}^{\overline{\overline{s}}} + \left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}} - \varepsilon^{\overline{\overline{ws}}}(\mathbf{I} - \mathbf{G}^{ws})\gamma^{ws}\right] : \mathbf{d}^{\overline{\overline{ws}}} \\
&- \sum_{\alpha \in \mathfrak{I}_{\mathrm{P}}} \sum_{i \in \mathfrak{I}_{s/N}} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \nabla \left(\mu^{\overline{i\alpha}} - \mu^{\overline{N\alpha}}\right) - \sum_{\alpha \in \mathfrak{I}_{\mathrm{P}}} \sum_{k \in \mathfrak{I}_{\mathrm{rxn}\alpha}} R^{k\alpha} A^{k\alpha} \\
&+ \left\{\nabla\left(\varepsilon^{\overline{\overline{w}}} p^{w}\right) - \sum_{i \in \mathfrak{I}_{s}} \varepsilon^{\overline{\overline{w}}} \rho^{w} \omega^{i\overline{w}} \left[\nabla\left(\mu^{\overline{iw}} + \psi^{\overline{w}}\right) + \mathbf{g}^{\overline{w}}\right] + \overset{w\to ws}{\mathbf{T}_{0}}\right\} \cdot \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right)
\end{aligned}$$

$$-\left\{\nabla\cdot\left[\varepsilon^{\overline{\overline{ws}}}\left(\mathbf{I}-\mathbf{G}^{ws}\right)\gamma^{ws}\right]+\overset{w\to ws}{\mathbf{T}_0}+\overset{s\to ws}{\mathbf{T}_0}\right\}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)$$

$$-\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\left(p_w^{ws}+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}+\gamma^{ws}J_s^{ws}\right)=\theta\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. \qquad (10.37)$$

10.6.2 Count of Equations and Variables

To be able to close the equation set that has been developed, the same number of equations and unknowns must exist. Therefore, it is important to count both of these quantities so that a strategy can be developed to eliminate the deficiency in equations.

With N being the number of species, we have $2N$ mass conservation equations, one for each species in the w and s phases. We have already made use of the mass conservation equation for the interface through Secondary Restriction 10.3 and the imposition of its consequences in Eq. (10.29). Because we are modeling momentum on an entity basis, we have three vector components of the momentum equations for the three entities, making a total of nine momentum equations. Because the system is isothermal, the energy equations for the entities are not needed. The body force potential equation does not need to be closed either since it pairs with the energy equation. If we include the SEI in the count, the total number of conservation and balance equations is $10+2N$.

The variables in these equations, denoted as members of the set $\mathcal{V}_0$, are as follows:

$$\begin{aligned}\mathcal{V}_0=\{&\varepsilon^{\overline{\overline{\alpha}}},\rho^{\kappa},\omega^{i\overline{\kappa}},\mathbf{v}^{\overline{\alpha}},\mathbf{u}^{\overline{\overline{i\kappa}}},r^{i\kappa},\mathbf{g}^{\overline{\kappa}},\overset{\kappa\to ws}{\mathbf{T}_0},\mathbf{t}^{\overline{\overline{\alpha}}},p^{w},p_w^{ws},\mathbf{t}^{s},\gamma^{ws},\\&\mathbf{G}^{ws},\mu^{\overline{i\kappa}},R^{m\kappa},A^{m\kappa},\psi^{\overline{w}},\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}},J_s^{ws},\Lambda^{\overline{\overline{\alpha}}}\}\\&\text{for }\alpha\in\mathfrak{J},\kappa\in\mathfrak{J}_{\mathrm{P}},i\in\mathfrak{J}_s,m\in\mathfrak{J}_{\mathrm{rxn}\kappa}\,.\end{aligned} \qquad (10.38)$$

A count of the scalar elements indicates that there are $80+12N+4N_{\mathrm{rxn}}$ members of $\mathcal{V}_0$. This count may be reduced by 15 by taking into account the fact that each of the five tensors is symmetric. A further reduction of 10 may be made because of the 10 scalar conditions,

$$\sum_{i\in\mathfrak{J}_s}\omega^{i\overline{\kappa}}=1 \quad \text{for } \kappa\in\mathfrak{J}_{\mathrm{P}}\,, \qquad (10.39)$$

$$\sum_{i\in\mathfrak{J}_s}\omega^{i\overline{\kappa}}\mathbf{u}^{\overline{\overline{i\kappa}}}=\mathbf{0} \quad \text{for } \kappa\in\mathfrak{J}_{\mathrm{P}}\,, \qquad (10.40)$$

and

$$\sum_{i\in\mathfrak{J}_s}r^{i\kappa}=0 \quad \text{for } \kappa\in\mathfrak{J}_{\mathrm{P}}\,. \qquad (10.41)$$

Thus, the number of variables that must be accounted for decreases to $55 + 12N + 4N_{\mathrm{rxn}}$.

As noted, we have $10 + 2N$ conservation and balance equations available, so we are in need of $45 + 10N + 4N_{\mathrm{rxn}}$ additional conditions. If we do not make use of the linearization opportunity provided by the product of reactions and affinity, the SEI still provides $25 + 6(N-1)$ closure relations from linearization of force-flux pairs. This reduces the number of excess variables further to $26 + 4N + 4N_{\mathrm{rxn}}$.

In Sect. 9.6.3, we found 29 conditions that could be applied to the single-phase-flow case. These conditions can be applied here with the exception of the equation of state for the chemical potential of the w phase, Eq. (9.70), because chemical potentials are posed on a species basis. Additionally, the equations of state might be modified in some cases to reflect dependence on composition. Nevertheless, we have identified 28 conditions so that the shortage in variables reduces to $4N - 2 + 4N_{\mathrm{rxn}}$.

This deficiency in variables can be overcome by posing equations of state for $\mu^{\overline{i\kappa}}$ for $i \in \mathfrak{I}_s, \kappa \in \mathfrak{I}_{\mathrm{P}}$. These equations of state might be analogous to those posed in Chap. 3 but expressed in terms of macroscale variables. This provides $2N$ conditions. Typically, the $2N_{\mathrm{rxn}}$ forms of $R^{m\kappa}$ are determined through laboratory experimentation. Combination of the stoichiometric coefficients with the chemical potentials then gives $2N_{\mathrm{rxn}}$ expressions for $A^{m\kappa}$. The remaining $2N - 2$ conditions are the relations between the mass rate of production, $r^{i\kappa}$, and the chemical reactions expressions as given by Eq. (10.30). Note that only $N - 1$ of these relations can be formed for each phase as the condition that the sum of the production rates must be zero has already been imposed in Eq. (10.41).

With the number of equations and unknowns equalized, it is possible to close the mass and momentum equations for isothermal transport without interphase transfer of mass. We will leave a demonstration of closure to a subsequent case.

10.7 Isothermal Transport with Interphase Mass Exchange

This case is more complex than the last because it allows for interphase mass exchange as modeled by the term $\overset{iw\to is}{M}$. The temperature is considered constant, so the energy transport equation does not have to be solved as part of the model.

10.7.1 Simplification of the SEI

For this case, the secondary restriction imposed is less restrictive than that of Secondary Restriction 10.5. It may be stated as:

Secondary Restriction 10.6 (Isothermal)
The system is constrained to be isothermal with no temperature gradients such that

$$\theta^{\overline{\overline{\alpha}}} = \theta^{\cdot} \quad for\ \alpha \in \mathfrak{I} \tag{10.42}$$

and

$$\nabla\theta^{\overline{\overline{\alpha}}} = 0 \quad for\ \alpha \in \mathfrak{I}\,. \tag{10.43}$$

The only difference between the SEI for this problem and Eq. (10.37) is that line 7 of SEI Eq. (10.33) must be retained. Thus, the SEI for this case is

$$\begin{aligned}
&\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{w}}}p^{w}\mathbf{I}\right):\mathbf{d}^{\overline{w}} + \left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right):\mathbf{d}^{\overline{s}} + \left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}} - \varepsilon^{\overline{\overline{ws}}}(\mathbf{I}-\mathbf{G}^{ws})\gamma^{ws}\right]:\mathbf{d}^{\overline{\overline{ws}}} \\
&- \sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\sum_{i\in\mathfrak{I}_{s/N}} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\nabla\left(\mu^{\overline{i\alpha}} - \mu^{\overline{N\alpha}}\right) - \sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\sum_{k\in\mathfrak{I}_{\mathrm{rxn}\alpha}} R^{k\alpha}A^{k\alpha} \\
&+ \sum_{i\in\mathfrak{I}_s} \overset{iw\to is}{M}\left[\mu^{\overline{iw}} + \psi^{\overline{w}} - \left(\mu^{\overline{is}} + \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^{s}}{3\rho^{s}j^{s}} + \psi^{\overline{s}}\right)\right] \\
&+ \left\{\nabla\left(\varepsilon^{\overline{\overline{w}}}p^{w}\right) - \sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\left[\nabla\left(\mu^{\overline{iw}} + \psi^{\overline{w}}\right) + \mathbf{g}^{\overline{w}}\right] + \overset{w\to ws}{\mathbf{T}_0}\right\}\cdot\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) \\
&- \left\{\nabla\cdot\left[\varepsilon^{\overline{\overline{ws}}}\left(\mathbf{I}-\mathbf{G}^{ws}\right)\gamma^{ws}\right] + \overset{w\to ws}{\mathbf{T}_0} + \overset{s\to ws}{\mathbf{T}_0}\right\}\cdot\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \\
&- \frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\left(p_{w}^{ws} + \langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}} + \gamma^{ws}J_{s}^{ws}\right) = \theta^{\cdot}\sum_{\alpha\in\mathfrak{I}}\Lambda^{\overline{\overline{\alpha}}} \geq 0\,.
\end{aligned} \tag{10.44}$$

10.7.2 Additional Variables and Constraints

The SEI of Eq. (10.44) contains variables that are properties of the solid phase as well as the mass exchange term that did not appear in the previous case. Furthermore, because the mass exchange term is retained, momentum conservation described by Eq. (6.201) also contains phase velocities and dispersion vectors integrated over the interface that previously did not have to be considered. The additional variables that must be accounted for comprise the set $\mathcal{V}_M$, where

$$\mathcal{V}_M = \{\overset{iw\to is}{M}, \psi^{\overline{s}}, \boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^{s}/j^{s}, \mathbf{v}_{\kappa}^{\overline{ws}}, \mathbf{u}_{i\kappa}^{\overline{ws}}\} \quad \text{for } \kappa \in \mathfrak{I}_{\mathrm{P}}, i \in \mathfrak{I}_s\,. \tag{10.45}$$

This set has $8+7N$ members. The line in Eq. (10.44) that contains $\overset{iw\to is}{M}$ suggests a path to linear closure of these exchange terms and thus provides N conditions. The body force potential for the solid, $\psi^{\overline{s}}$, can be treated in the same way as $\psi^{\overline{w}}$, as discussed in Sect. 9.6.3. The grouping $\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^{s}/j^{s}$ is dealt with through its relation to the solid-phase stress tensor and the elastic properties of the solid. The flow and diffusion terms at the *ws* interface are the remaining $6+6N$ unknown variables. Both variables appear in momentum equation $\mathcal{P}_{**}^{\overline{\overline{\alpha}}}$ for $\alpha \in \mathfrak{I}$, Eq. (6.201), multiplying the mass exchange term. They only appear as a sum, so they need not be specified individually. Rather, only $\mathbf{v}_{\kappa}^{\overline{ws}} + \mathbf{u}_{i\kappa}^{\overline{ws}}$ needs to be accounted for. This species velocity appears in a term that is of order velocity squared, which is typically negligible for modeling the momentum of flows in porous media. Thus, as a first approximation, $\mathbf{v}_{\kappa}^{\overline{ws}} + \mathbf{u}_{i\kappa}^{\overline{ws}}$ can be eliminated from the formulation.

The additional unknowns associated with interphase exchange thus do not add a significant burden to the formulation. The mass exchange term will be related to the difference in the potentials in the fluid and solid phases. Subsequently, this will be written explicitly when showing the closure relations for interphase transport in the non-isothermal case.

10.8 Unitemperature, Nonisothermal Transport

This case considers heat and mass transport in a porous medium. The transport of energy is modeled most simply using a macroscale local equilibrium assumption for temperature. By this assumption, temperature gradients may exist within the system, but the average temperature within an averaging volume is independent of the entity. With such a model, energy transport equations must be included, but only one temperature field must be determined.

10.8.1 Simplification of the SEI for a Single Temperature

For this model, the secondary restriction that is imposed on Eq. (10.33) may be stated:

Secondary Restriction 10.7 (Isothermal)
The system is restricted to the case where the temperature of each entity is the same at each point, but the gradient in temperature may be non-zero such that

$$\theta^{\overline{\overline{\alpha}}} = \theta^{\cdot} \quad \textit{for } \alpha \in \mathfrak{I} \, . \tag{10.46}$$

For this model, lines 8–11 of Eq. (10.33) are eliminated because the forces consisting of temperature differences are zero.

For the single temperature model, in anticipation of linear closure, the SEI simplifies to

$$\frac{1}{\theta^{\cdot}}\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{w}}} p^{w}\mathbf{I}\right) : \mathbf{d}^{\overline{\overline{w}}} + \frac{1}{\theta^{\cdot}}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right) : \mathbf{d}^{\overline{\overline{s}}} + \frac{1}{\theta^{\cdot}}\left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}} - \varepsilon^{\overline{\overline{ws}}}(\mathbf{I} - \mathbf{G}^{ws})\gamma^{ws}\right] : \mathbf{d}^{\overline{\overline{ws}}}$$

$$
\begin{aligned}
&- \sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}} \left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\alpha}}} + \sum_{i\in\mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mu^{\overline{i\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}} \right)\cdot\nabla\left(\frac{1}{\theta^{\cdot}}\right) - \varepsilon^{\overline{\overline{ws}}}\mathbf{q}^{\overline{\overline{ws}}}\cdot\nabla\left(\frac{1}{\theta^{\cdot}}\right) \\
&- \sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}} \sum_{i\in\mathfrak{I}_{s/N}} \frac{1}{\theta^{\cdot}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\nabla\left(\mu^{\overline{i\alpha}} - \mu^{\overline{N\alpha}}\right) - \sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}} \sum_{k\in\mathfrak{I}_{\mathrm{rxn}\alpha}} \frac{1}{\theta^{\cdot}}R^{k\alpha}A^{k\alpha} \\
&+ \sum_{i\in\mathfrak{I}_s} \frac{1}{\theta^{\cdot}} \overset{iw\rightarrow is}{M} \left[\mu^{\overline{iw}} + \psi^{\overline{w}} - \left(\mu^{\overline{is}} + \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^{s}}{3\rho^{s}j^{s}} + \psi^{\overline{s}} \right) \right] \\
&- \frac{1}{\theta^{\cdot}} \left\{ \eta^{\overline{\overline{w}}}\nabla\theta^{\cdot} - \nabla\left(\varepsilon^{\overline{\overline{w}}}p^{w}\right) + \sum_{i\in\mathfrak{I}_s} \varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}} \left[\nabla\left(\mu^{\overline{iw}} + \psi^{\overline{w}}\right) + \mathbf{g}^{\overline{w}} \right] \right. \\
&\qquad \left. - \overset{w\rightarrow ws}{\mathbf{T}_0} \right\} \cdot \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) \\
&- \frac{1}{\theta^{\cdot}} \left\{ \eta^{\overline{\overline{ws}}}(\mathbf{I} - \mathbf{G}^{ws})\cdot\nabla\theta^{\cdot} + \nabla\cdot\left[\varepsilon^{\overline{\overline{ws}}}(\mathbf{I} - \mathbf{G}^{ws})\,\gamma^{ws}\right] + \overset{w\rightarrow ws}{\mathbf{T}_0} + \overset{s\rightarrow ws}{\mathbf{T}_0} \right\} \cdot \left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) \\
&- \frac{1}{\theta^{\cdot}} \frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} \left(p_{w}^{ws} + \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}} + \gamma^{ws}J_{s}^{ws} \right) = \sum_{\alpha\in\mathfrak{I}} \Lambda^{\overline{\overline{\alpha}}} \geq 0\,. \qquad (10.47)
\end{aligned}
$$

10.8.2 Accounting for Additional Variables

The variables in addition to those listed previously include those in Eq. (10.47) that multiply the temperature gradient. These are associated with non-advective energy fluxes and entropy. Additionally, the variables in the equation for conservation of energy, Eq. (6.203), that have not already been accounted for must be considered. This case of non-constant temperature requires that the energy equation be part of the system model. This expansion to the set of variables is denoted as $\mathcal{V}_E$ where

$$\mathcal{V}_E = \{\theta^{\cdot}, \eta^{\overline{\overline{w}}}, \eta^{\overline{\overline{ws}}}\mathbf{q}^{\overline{\overline{\alpha}}}, \mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\kappa}}}, E^{\overline{\overline{\alpha}}}, h_{0}^{\overline{\overline{\alpha}}}, h^{\alpha}, \overline{E}_{i\kappa}^{\overline{ws}}\} \quad \text{for } \alpha\in\mathfrak{I}, \kappa\in\mathfrak{I}_{\mathrm{P}}, i\in\mathfrak{I}_s\,. \qquad (10.48)$$

This set has 27+2N members. We will assume there are no body sources of energy so that

$$h^{\alpha} = 0 \quad \text{for } \alpha\in\mathfrak{I}\,. \qquad (10.49)$$

As defined by Eqs. (6.104) and (6.190), when the gravity vector is independent of species,

$$h_{0}^{\overline{\overline{\alpha}}} = 0 \quad \text{for } \alpha\in\mathfrak{I}\,. \qquad (10.50)$$

Here, we will consider $\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\kappa}}}$ defined in Eqs. (6.154) and (6.199) to be negligible such that

$$\mathbf{q}_{\mathbf{g}0}^{\overline{\overline{\kappa}}} = 0 \quad \text{for } \kappa\in\mathfrak{I}_{\mathrm{P}}\,. \qquad (10.51)$$

We also assume that equations of state can be developed for the macroscale energy functions, $E^{\overline{\overline{\alpha}}}$ and $\hat{E}^{\overline{\overline{ws}}}_{i\kappa}$, and the macroscale entropies, $\eta^{\overline{\overline{w}}}$ and $\eta^{\overline{\overline{ws}}}$. This leaves the nine components of $\mathbf{q}^{\overline{\overline{\alpha}}}$ and the temperature as the remaining unknowns. We need 10 more conditions.

Before we determine the source of these 10 conditions, we will rearrange some terms, not because this is necessary but because it is informative in terms of showing an approximation that underpins a classical result. We assume that the microscale expression derived in Eq. (5.34) can be written in terms of macroscale variables as an approximate equation,

$$\nabla \mu^{\overline{i\alpha}} = \nabla \mu^{\overline{i\alpha}}\Big|_{\theta^{\overline{\overline{\alpha}}}} + \theta^{\overline{\overline{\alpha}}} \left(\overline{H}^{\overline{i\alpha}} - \mu^{\overline{i\alpha}} \right) \nabla \left(\frac{1}{\theta^{\overline{\overline{\alpha}}}} \right) . \tag{10.52}$$

This relation may be used in conjunction with the dispersion term in Eq. (10.47). We make use of this relation, Eq. (10.51), and the fact that temperatures of all entities are equal so that terms on the left side of the following equality, taken from Eq. (10.47), can be re-expressed on the right side according to

$$\begin{aligned}
&- \sum_{\alpha \in \mathfrak{I}_{\mathrm{P}}} \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} + \sum_{i \in \mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \mu^{\overline{i\alpha}} \mathbf{u}^{\overline{\overline{i\alpha}}} \right) \cdot \nabla \left(\frac{1}{\theta} \right) - \varepsilon^{\overline{\overline{ws}}} \mathbf{q}^{\overline{\overline{ws}}} \cdot \nabla \left(\frac{1}{\theta} \right) \\
&\quad - \sum_{\alpha \in \mathfrak{I}_{\mathrm{P}}} \sum_{i \in \mathfrak{I}_{s/N}} \frac{1}{\theta} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \nabla \left(\mu^{\overline{i\alpha}} - \mu^{\overline{N\alpha}} \right) = \\
&- \left[\sum_{\alpha \in \mathfrak{I}_{\mathrm{P}}} \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} + \sum_{i \in \mathfrak{I}_s} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \overline{H}^{\overline{i\alpha}} \right) + \varepsilon^{\overline{\overline{ws}}} \mathbf{q}^{\overline{\overline{ws}}} \right] \cdot \nabla \left(\frac{1}{\theta} \right) \\
&\quad - \sum_{\alpha \in \mathfrak{I}_{\mathrm{P}}} \sum_{i \in \mathfrak{I}_{s/N}} \frac{1}{\theta} \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \omega^{i\overline{\alpha}} \mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \nabla \left(\mu^{\overline{i\alpha}}\Big|_{\theta} - \mu^{\overline{N\alpha}}\Big|_{\theta} \right) .
\end{aligned} \tag{10.53}$$

Substitution of this equality into the SEI Eq. (10.47) provides a force-flux pairing that can be employed in closing the non-advective energy transport and the species dispersion.

Because the temperatures in all entities are equal, the quantity in brackets on the right side of Eq. (10.53) is treated as a single vector flux that can be obtained based on a linearization of the SEI (i.e., we will be able to get closure approximations for three aggregate vector components). We are unable to obtain the non-advective heat flux vectors for each entity separately. This suggests that, rather than using Eq. (6.203) for the energy of each entity, we sum this equation over all entities to obtain a single energy equation that contains the same sum of the non-advective energy fluxes that appears in the SEI. Additionally, all inter-entity energy exchanges cancel out when the energy equation is summed over all entities. This summing reduces the number of unknowns from the nine elements of $\mathbf{q}^{\overline{\overline{\alpha}}}$ for $\alpha \in \mathfrak{I}$ to the three members of the combined heat flux expression. Expressions for closure of these elements are suggested by the SEI. The combined energy equation provides the final condition needed to have a closed set of equations.

The consequence of the single temperature model is that one is able to use a single energy equation to model energy transport in the system. The model requires constitutive relations for partial mass energy, enthalpy, and chemical potential of each species. At the microscale, this thermodynamic information is often available. For a macroscale model, one must be careful and realize that the equations of state must be scaled up to account for variability of thermodynamic quantities within the averaging volume. This creates challenges in being able to close a model reliably.

10.9 Multi-temperature Species Transport

This is the most complex model to be considered in this chapter. It allows for flow and chemical species transport within and between phases. Additionally, the system is considered to be non-isothermal with temperature gradients within the phases as well as a temperature difference between phases that drives interphase energy transport. The models considered in the previous three sections are special cases of this more general model. However, even this model incorporates some simplifications to the SEI of Eq. (10.33). We will indicate the simplifications and develop the closed model.

10.9.1 SEI for the Multi-temperature Case

The SEI to be employed here is based on Eq. (10.33) with limited simplification. Terms involving $\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}$ or $\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}}$ are dropped as being of second-order smallness. Additionally, Eq. (10.52) will be used in lines 3–5 of Eq. (10.33) to separate out the elements of dispersion that are due to thermal effects.[4] The reduced form of the SEI with these assumptions applied is

$$\begin{aligned}
&\frac{1}{\theta^{\overline{\overline{\overline{w}}}}}\left(\varepsilon^{\overline{\overline{w}}}\mathbf{t}^{\overline{\overline{w}}}+\varepsilon^{\overline{\overline{w}}}p^{w}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{w}}}+\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}} && 1\\
&+\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\left[\varepsilon^{\overline{\overline{ws}}}\mathbf{t}^{\overline{\overline{ws}}}-\varepsilon^{\overline{\overline{ws}}}(\mathbf{I}-\mathbf{G}^{ws})\gamma^{ws}\right]:\mathbf{d}^{\overline{\overline{ws}}} && 2\\
&-\sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\sum_{i\in\mathfrak{I}_{s}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\overline{H}^{\overline{i\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right)\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\right)-\varepsilon^{\overline{\overline{ws}}}\mathbf{q}^{\overline{\overline{ws}}}\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\overline{ws}}}}}\right) && 3\\
&-\sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\sum_{i\in\mathfrak{I}_{s/N}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\nabla\left(\mu^{\overline{i\alpha}}\Big|_{\theta^{\overline{\overline{\overline{\alpha}}}}}-\mu^{\overline{N\alpha}}\Big|_{\theta^{\overline{\overline{\overline{\alpha}}}}}\right) && 4
\end{aligned}$$

---

[4] It is also possible to use Eq. (10.52) to replace all the gradients of chemical potential that appear in Eq. (10.33). This provides an interesting rearrangement of the multiplier of $\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}$ by allowing $\eta^{\overline{\overline{\overline{w}}}}\nabla\theta^{\overline{\overline{\overline{w}}}}$ to be eliminated. Of course neither of these rearrangements is required for closing the model!

$$
\begin{aligned}
&-\sum_{\alpha\in\mathfrak{J}_{\mathrm{P}}}\ \sum_{k\in\mathfrak{J}_{\mathrm{rxn}\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} R^{k\alpha}A^{k\alpha} \\
&+\sum_{i\in\mathfrak{J}_s} \overset{iw\to is}{M} \left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{iw}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{is}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}\mathbf{:}\mathsf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{s}}\right)\right] \\
&-\left\{\overset{w\to ws}{Q_1}+\overset{w\to ws}{G_0}+\sum_{i\in\mathfrak{J}_s}\left(\overline{E}^{\overline{ws}}_{iw}+\psi^{\overline{ws}}_{w}\right)\overset{iw\to is}{M}+p^{ws}_{w}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\right\}\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right) \\
&-\left\{\overset{s\to ws}{Q_1}+\overset{s\to ws}{G_0}-\sum_{i\in\mathfrak{J}_s}\left(\overline{E}^{\overline{ws}}_{is}+\psi^{\overline{ws}}_{s}\right)\overset{iw\to is}{M}\right. \\
&\qquad\left.+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\right\}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right) \\
&-\frac{1}{\theta^{\overline{\overline{w}}}}\left\{\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}}-\nabla\left(\varepsilon^{\overline{\overline{w}}}p^{w}\right)+\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\left[\nabla\left(\mu^{\overline{iw}}+\psi^{\overline{w}}\right)+\mathbf{g}^{\overline{w}}\right]\right. \\
&\qquad\left.-\overset{w\to ws}{\mathbf{T}_0}\right\}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right) \\
&-\frac{1}{\theta^{\overline{\overline{ws}}}}\left\{\eta^{\overline{\overline{ws}}}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\cdot\nabla\theta^{\overline{\overline{ws}}}+\nabla\cdot\left[\varepsilon^{\overline{\overline{ws}}}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\gamma^{ws}\right]\right. \\
&\qquad\left.+\overset{w\to ws}{\mathbf{T}_0}+\overset{s\to ws}{\mathbf{T}_0}\right\}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right) \\
&-\frac{1}{\theta^{\overline{\overline{ws}}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\left(p^{ws}_{w}+\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}+\gamma^{ws}J^{ws}_{s}\right)=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,.
\end{aligned}
\tag{10.54}
$$

10.9.2 Treatment of Additional Variables

The variables that enter the analysis, in addition to those discussed in the previous sections, are two temperatures, indicated as those of the *s* and *ws* entities, and the fluxes of energy at the boundary between entities. This set is denoted as $\mathcal{V}_Q$, where

$$
\mathcal{V}_Q=\{\theta^{\overline{\overline{s}}},\theta^{\overline{\overline{ws}}},\overset{\kappa\to ws}{Q_1},\overset{\kappa\to ws}{G_0}\}\quad\text{for }\kappa\in\mathfrak{J}_{\mathrm{P}}\,. \tag{10.55}
$$

This set contains six variables; thus, we need six additional conditions to be able to close the system. Because we are allowing the entities to have different temperatures, energy conservation as described by Eq. (6.203) is formulated separately for each entity. In the single temperature model, we made use of one energy equation, the sum of the three entity equations. By not combining them, we are able to reduce the equation deficit by two. The quantity $\overset{\kappa\to ws}{G_0}$ is defined in Eq. (6.198) as the sum over all species of $\overset{i\kappa\to iws}{G_0}$, defined in Eqs. (6.156) and (6.156). In essence, $\overset{\kappa\to ws}{G_0}$ involves a product of a difference in gravitational potentials, one averaged over a phase and the other averaged over the boundary of the phase, multiplied by a mass exchange term, a force in the force-flux relation of the SEI given by Eq. (10.54). Since it also multiplies a temperature difference force, it may be dropped as being of higher order smallness. Thus, we approximate

$$\overset{\kappa\to ws}{G_0} = 0 \quad \text{for } \kappa \in \mathfrak{I}_{\mathrm{P}} \, . \tag{10.56}$$

This leaves two variables, $\overset{w\to ws}{Q_1}$ and $\overset{s\to ws}{Q_1}$, which can be approximated using linearized closure relations motivated by the SEI.

10.10 Example of Conjugate Force-flux Closure

A general approach to closing the conservation equations based on Eq. (10.54) can include a number of processes, such as coupling between non-advective heat and mass transport and interactions among dispersing chemical species. These topics make use of cross-coupling, as demonstrated at the microscale in Sect. 5.9. Our objective here is not to provide an exhaustive illustration of TCAT examples, but to provide the important elements of the framework as displayed in Fig. 1.3. This goal can be accomplished by examining an admittedly simplified, but nevertheless compelling, example of closure at the macroscale. The intricacies of cross-coupling provide a fertile ground for study, especially for larger-scale system descriptions, with microscale illustrations available in the literature [e.g., 1, 2, 4–7].

Here, we will consider a system with the following characteristics and restrictions that guide the closure of the system described based on the SEI of Eq. (10.54) and the antecedent primary and secondary restrictions.

Closure Approximation 10.1 (Species and Interactions)
The single-fluid-phase porous medium system that is transporting heat and mass is restricted as follows

- *the w phase is composed of two chemical species denoted as A and B;*
- *the s phase is composed of two chemical species denoted as A and C;*
- *only species A is exchanged between the w and s phases;*
- *all species may react reversibly within their phases such that A reacts to form B in the w phase and A reacts to form C in the solid phase, and vice-versa;*
- *the temperatures of the phases and of the massless interface are not necessarily equal;*
- *the concentration of solute A and the temperature gradients are small enough that coupling between heat and mass transfer may be neglected;*
- *no coupling between phases exists for intraphase processes; and*

- *coupling of dispersion to the flow velocities may be neglected.*

A consequence of the stated approximation is that cross-coupling of forces may be ignored in formulating closure relations.

10.10.1 Closure Relations

The closure relations here proceed from Eq. (10.54) subject to Closure Approximation 10.1. We assume that the fluxes that multiply rate of strain tensors are zero order in those tensors. All other fluxes are treated as being linearly proportional to their conjugate forces. The assumption that the stresses are zero order in the rates of strain is consistent with the expectation that viscous type forces evidence themselves at the microscale but not at the macroscale. The assumptions made are the simplest that can be proposed that match the physics of some systems.

Forces: $\mathbf{d}^{\overline{\overline{w}}}$, $\mathbf{d}^{\overline{\overline{s}}}$, $\mathbf{d}^{\overline{\overline{ws}}}$

Making use of the assumption of zero order dependence of fluxes on these forces, we obtain the equations for the stress tensors from lines 1 and 2 of Eq. (10.54) as

$$\mathsf{t}^{\overline{\overline{w}}} = -p^w \mathsf{I} \, , \tag{10.57}$$

$$\mathsf{t}^{\overline{\overline{s}}} = \mathsf{t}^s \, , \tag{10.58}$$

and

$$\mathsf{t}^{\overline{\overline{ws}}} = \gamma^{ws} \left(\mathsf{I} - \mathsf{G}^{ws} \right) \, . \tag{10.59}$$

These equations are the same as those for the single-fluid-flow system in Eqs. (9.74)–(9.76).

Forces: $\nabla\left(\frac{1}{\theta^{\overline{\overline{w}}}}\right)$, $\nabla\left(\frac{1}{\theta^{\overline{\overline{s}}}}\right)$, $\nabla\left(\frac{1}{\theta^{\overline{\overline{ws}}}}\right)$

These forces appear in line 3 of Eq. (10.54). For the phases we obtain the closure relations for the non-advective heat fluxes from line 3 as

$$\mathbf{q}^{\overline{\overline{w}}} + \rho^w \omega^{A\overline{w}} (\overline{H}^{\overline{Aw}} - \overline{H}^{\overline{Bw}}) \mathbf{u}^{\overline{\overline{Aw}}} = -\hat{\mathsf{k}}^w_\theta \cdot \nabla \left(\frac{1}{\theta^{\overline{\overline{w}}}} \right) \tag{10.60}$$

and

$$\mathbf{q}^{\overline{\overline{s}}} + \rho^s \omega^{A\overline{s}} (\overline{H}^{\overline{As}} - \overline{H}^{\overline{Cs}}) \mathbf{u}^{\overline{\overline{As}}} = -\hat{\mathsf{k}}^s_\theta \cdot \nabla \left(\frac{1}{\theta^{\overline{\overline{s}}}} \right) \, . \tag{10.61}$$

In writing these equations, we have made use of the facts that

$$\omega^{A\overline{w}}\mathbf{u}^{\overline{\overline{Aw}}} = -\omega^{B\overline{w}}\mathbf{u}^{\overline{\overline{Bw}}} \tag{10.62}$$

and

$$\omega^{A\overline{s}}\mathbf{u}^{\overline{\overline{As}}} = -\omega^{C\overline{s}}\mathbf{u}^{\overline{\overline{Cs}}} \,. \tag{10.63}$$

For the interface, linearization of the non-advective heat flux in line 3 of Eq. (10.54) gives

$$\mathbf{q}^{\overline{\overline{ws}}} = -\hat{\mathsf{k}}_{\theta}^{ws}\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{ws}}}}\right) \,. \tag{10.64}$$

The coefficient tensors $\hat{\mathsf{k}}_{\theta}^{\alpha}$ are positive and semi-definite. When the corresponding entities are isotropic, these tensors are scalars.

Forces: $\nabla\left(\mu^{\overline{Aw}}\Big|_{\theta^{\overline{w}}} - \mu^{\overline{Bw}}\Big|_{\theta^{\overline{w}}}\right)$, $\nabla\left(\mu^{\overline{As}}\Big|_{\theta^{\overline{s}}} - \mu^{\overline{Cs}}\Big|_{\theta^{\overline{s}}}\right)$

For an entity consisting of N chemical species, there are $N-1$ independent dispersion vectors. Thus, for the present case where each phase has two species, line 4 of entropy inequality Eq. (10.54) suggests one linearized dispersion vector for each phase with

$$\omega^{A\overline{w}}\mathbf{u}^{\overline{\overline{Aw}}} = -\hat{\mathsf{D}}_{AB}^{w}\cdot\nabla\left(\mu^{\overline{Aw}}\Big|_{\theta^{\overline{w}}} - \mu^{\overline{Bw}}\Big|_{\theta^{\overline{w}}}\right) \tag{10.65}$$

and

$$\omega^{A\overline{s}}\mathbf{u}^{\overline{\overline{As}}} = -\hat{\mathsf{D}}_{AC}^{s}\cdot\nabla\left(\mu^{\overline{As}}\Big|_{\theta^{\overline{s}}} - \mu^{\overline{Cs}}\Big|_{\theta^{\overline{s}}}\right) \,, \tag{10.66}$$

where the binary dispersion coefficients, $\hat{\mathsf{D}}_{AB}^{w}$ and $\hat{\mathsf{D}}_{AC}^{s}$, reduce to scalars if the dispersion process is isotropic. In obtaining these relations, we selected species B as the reference species in the w phase and species C as the reference species in the s phase.

Equations (10.62) and (10.63) can be employed to obtain the dispersion vectors for species B and C, respectively, from Eqs. (10.65) and (10.66) as

$$\omega^{B\overline{w}}\mathbf{u}^{\overline{\overline{Bw}}} = -\hat{\mathsf{D}}_{AB}^{w}\cdot\nabla\left(\mu^{\overline{Bw}}\Big|_{\theta^{\overline{w}}} - \mu^{\overline{Aw}}\Big|_{\theta^{\overline{w}}}\right) \tag{10.67}$$

and

$$\omega^{C\overline{s}}\mathbf{u}^{\overline{\overline{Cs}}} = -\hat{\mathsf{D}}_{AC}^{s}\cdot\nabla\left(\mu^{\overline{Cs}}\Big|_{\theta^{\overline{s}}} - \mu^{\overline{As}}\Big|_{\theta^{\overline{s}}}\right) \,. \tag{10.68}$$

Forces: $A^{k\alpha}$

The strategy that follows from a linearization of line 5 of Eq. (10.54) is an approximation of the chemical reaction as

$$R^{k\alpha} = -\hat{K}_{k\alpha} A^{k\alpha} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}}, k \in \mathfrak{I}_{\mathrm{rxn}\alpha} \,. \tag{10.69}$$

Then from this expression the production rate of each species can be developed from Eq. (10.30). However, instead of this approach, it is much more common to postulate chemical reaction rate expressions based on laboratory analyses. When systems have many components, the business of obtaining reasonable expressions for reaction rates can be very difficult.

For the case of a monomolecular, first-order reaction, specifying an appropriate form for $R^{k\alpha}$ can be straightforward. For polymolecular reactions, complications arise and some subtle issues exist. Consider an example reaction whereby E and F react to form D according to

$$\mathrm{E} + \mathrm{F} \rightarrow \mathrm{D}. \tag{10.70}$$

Suppose the study of this reaction in a well-mixed laboratory system indicates that the rate is proportional to the concentrations of E and F. The issue that arises in specifying the reaction in a macroscale porous medium system is that the observed rate of reaction is not apt to be well-represented by the average concentrations because the reaction rate depends on the product of reactant concentrations. To demonstrate this consider an REV in which half of the domain has solute E but no solute F, and the other half of the domain has solute F but no solute E. Because the reactants are not in contact with each other, the rate of production of D would be zero. However using averaged concentrations over the REV in the developed rate expression, a non-zero rate of reaction would be calculated. Thus, the issue of scale emerges for this example and for all cases where a reaction is not zero or first order.

Accurate representation of biogeochemical reactions is an open issue and is problem dependent. Various approaches are possible for constructing models that represent the underlying system with adequate resolution. The first approach is to rely upon averaged values for computing reaction rates, but to resolve the discrete model adequately in regions where concentration gradients of the reactive species exist. Because diffusion and dispersion are operative phenomena in a porous medium system, some mixing will occur and grid resolution in appropriate locations will improve the accuracy of a computationally-predicted reaction rate. A second approach is to examine the limit where the rate of mixing determines the reaction rate and approximate the mixing rate based upon the dispersion tensor and local concentration gradients. More complicated multiscale modeling approaches are also possible where pore-scale modeling is coupled to a macroscale model.

The essential point is that use of a linearization procedure based on line 5 of the SEI is often inadequate as a model of a chemical reaction. Similarly, reaction rates $r_{i\alpha}$ determined in a laboratory based on well-mixed systems may not scale correctly for use in macroscale equations by averaging to obtain $r^{i\alpha}$. It should not be surprising that processes that are found to be non-linear may be represented poorly using a linear approximation.

Force: $\boldsymbol{\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{Aw}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{As}}+\frac{\sigma^{\overline{\overline{s}}}{:}\mathbf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{s}}\right)}$

The system is defined so that only chemical species A is transferred between the *w* and *s* entities. Therefore, from line 6 of Eq. (10.54) we obtain the linearized relation

$$\overset{Aw\to As}{M}=\hat{K}_{M}^{A}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{Aw}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{As}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{s}}\right)\right]\,, \tag{10.71}$$

where K_{M}^{A} is a non-negative coefficient. Also, Closure Approximation 10.1 requires that

$$\overset{Bw\to Bs}{M}=0 \tag{10.72}$$

and

$$\overset{Cw\to Cs}{M}=0\,. \tag{10.73}$$

Forces: $\boldsymbol{\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right),\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)}$

The temperature difference forces apply to lines 7 and 8–9 of Eq. (10.54). When the approximation of Eq. (10.56) is employed, the linearized relations for energy transfer between the phases and the interface are

$$\overset{w\to ws}{Q_1}=\left(\overline{E}_{Aw}^{\overline{ws}}+\psi_{w}^{\overline{ws}}\right)\overset{Aw\to As}{M}-p_{w}^{ws}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}-\hat{K}_{E}^{w}\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right) \tag{10.74}$$

and

$$\begin{aligned}\overset{s\to ws}{Q_1}=&-\left(\overline{E}_{As}^{\overline{ws}}+\psi_{s}^{\overline{ws}}\right)\overset{Aw\to As}{M}-\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}}\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t}\\&-\hat{K}_{E}^{s}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\,.\end{aligned} \tag{10.75}$$

Note that $\overset{Aw\to As}{M}$ in these equations may be replaced by Eq. (10.71).

Forces: $(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}})$, $(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}})$

The relative velocities are the driving forces in lines 10–13. Linearization of the fluxes around these forces gives the closure relations

$$\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}} - \nabla(\varepsilon^{\overline{\overline{w}}} p^{w}) + \sum_{i\in\{A,B\}} \varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\left[\nabla\left(\mu^{\overline{iw}} + \psi^{\overline{w}}\right) + \mathbf{g}^{\overline{w}}\right] - \overset{w\to ws}{\mathbf{T}_0}$$
$$= -\hat{\mathbf{R}}^{w}\cdot(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}) \tag{10.76}$$

and

$$\eta^{\overline{\overline{ws}}}\left(\mathbf{I} - \mathbf{G}^{ws}\right)\cdot\nabla\theta^{\overline{\overline{ws}}} + \nabla\cdot\left[\varepsilon^{\overline{\overline{ws}}}\left(\mathbf{I} - \mathbf{G}^{ws}\right)\gamma^{ws}\right] + \overset{w\to ws}{\mathbf{T}_0} + \overset{s\to ws}{\mathbf{T}_0}$$
$$= -\hat{\mathbf{R}}^{ws}\cdot(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}})\,. \tag{10.77}$$

The tensors $\hat{\mathbf{R}}^{w}$ and $\hat{\mathbf{R}}^{ws}$ are positive, semi-definite and simplify to non-negative scalar coefficients when the medium is isotropic.

Force: $p_{w}^{ws} + \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}} + \gamma^{ws}J_{s}^{ws}$

This driving force in line 14 of Eq. (10.54) is a disequilibrium of the forces at the surface of the solid phase. This can cause the matrix to deform so that the solid volume fraction will change. The linearization of the conjugate force gives

$$\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{s}}}{\mathrm{D}t} = -\hat{c}\left(p_{w}^{ws} + \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\rangle_{\Omega_{ws},\Omega_{ws}} + \gamma^{ws}J_{s}^{ws}\right)\,, \tag{10.78}$$

where $\hat{c}$ is a non-negative coefficient.

10.10.2 Closed Set of Conservation Equations

The closure relations of the last subsection can be used in conjunction with conservation equations for chemical species in each phase, momentum equations for each entity, and the energy equation for each entity, as indicated in Table 10.1. When employing the closure relations in the equations, it is important to apply the various assumptions and conditions that have been invoked in forming the SEI and the closure relations so that the assumptions are applied uniformly to the equation set. The results will be collected here.

Species Conservation in *w* and *s* Phases

Because ρ^{ws} has been set to zero and the condition that only the A species is exchanged between phases, four mass conservation equations are needed. These are obtained from Eq. (6.74), subject to closure conditions Eqs. (10.65)–(10.68) and Eqs. (10.71)–(10.73), as

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{w}}(\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{A\overline{w}})}{\mathrm{D}t}+\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{A\overline{w}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{w}}}-\nabla\cdot\left[\varepsilon^{\overline{\overline{w}}}\rho^{w}\hat{\mathsf{D}}^{w}_{AB}\cdot\nabla\left(\mu^{\overline{Aw}}\Big|_{\theta^{\overline{\overline{w}}}}-\mu^{\overline{Bw}}\Big|_{\theta^{\overline{\overline{w}}}}\right)\right]\\&\quad-\varepsilon^{\overline{\overline{w}}}r^{Aw}+\hat{K}^{A}_{M}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{Aw}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{As}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathsf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{s}}\right)\right]=0\,,\end{aligned}\tag{10.79}$$

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{w}}(\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{B\overline{w}})}{\mathrm{D}t}+\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{B\overline{w}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{w}}}-\nabla\cdot\left[\varepsilon^{\overline{\overline{w}}}\rho^{w}\hat{\mathsf{D}}^{w}_{AB}\cdot\nabla\left(\mu^{\overline{Bw}}\Big|_{\theta^{\overline{\overline{w}}}}-\mu^{\overline{Aw}}\Big|_{\theta^{\overline{\overline{w}}}}\right)\right]\\&-\varepsilon^{\overline{\overline{w}}}r^{Bw}=0\,,\end{aligned}\tag{10.80}$$

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{A\overline{s}})}{\mathrm{D}t}+\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{A\overline{s}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}}-\nabla\cdot\left[\varepsilon^{\overline{\overline{s}}}\rho^{s}\hat{\mathsf{D}}^{s}_{AC}\cdot\nabla\left(\mu^{\overline{As}}\Big|_{\theta^{\overline{\overline{s}}}}-\mu^{\overline{Cs}}\Big|_{\theta^{\overline{\overline{s}}}}\right)\right]\\&\quad-\varepsilon^{\overline{\overline{s}}}r^{As}-\hat{K}^{A}_{M}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{Aw}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{As}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathsf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{s}}\right)\right]=0\,,\end{aligned}\tag{10.81}$$

and

$$\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{C\overline{s}})}{\mathrm{D}t}+\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{C\overline{s}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}}-\nabla\cdot\left[\varepsilon^{\overline{\overline{s}}}\rho^{s}\hat{\mathsf{D}}^{s}_{AC}\cdot\nabla\left(\mu^{\overline{Cs}}\Big|_{\theta^{\overline{\overline{s}}}}-\mu^{\overline{As}}\Big|_{\theta^{\overline{\overline{s}}}}\right)\right]-\varepsilon^{\overline{\overline{s}}}r^{Cs}=0\,.\tag{10.82}$$

The rates of production in these equations will be approximated by chemical reaction expressions as discussed previously. For the system as constrained here, $r^{Aw}=-r^{Bw}$ and $r^{As}=-r^{Cs}$.

Momentum Conservation for *w*, *ws*, and *s* Entities

The momentum equations for the entities of this system are particular forms of Eq. (6.201). We use closure relations Eqs. (10.57)–(10.59) for the stress tensors and Eqs. (10.76) and (10.77) for the momentum exchange terms. The momentum equations for the *w*, *ws*, and *s* entities are, respectively,

$$\begin{aligned}&\frac{\mathrm{D}^{\overline{w}}}{\mathrm{D}t}\left(\varepsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{v}^{\overline{w}}\right)+\varepsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{v}^{\overline{w}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{w}}}\\&\quad+\hat{K}^{A}_{M}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{Aw}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{As}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathsf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{s}}\right)\right]\left(\mathbf{v}^{\overline{ws}}_{w}+\mathbf{u}^{\overline{ws}}_{Aw}\right)\end{aligned}$$

$$+\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}}+\sum_{i\in\{A,B\}}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\nabla\left(\mu^{\overline{iw}}+\psi^{\overline{w}}\right)+\hat{\mathsf{R}}^{w}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)=0\,, \tag{10.83}$$

$$\eta^{\overline{\overline{ws}}}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\cdot\nabla\theta^{\overline{\overline{ws}}}+\hat{\mathsf{R}}^{ws}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)=\mathbf{0}\,, \tag{10.84}$$

and

$$\begin{aligned}
&\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(\varepsilon^{\overline{\overline{s}}}\rho^{s}\mathbf{v}^{\overline{s}}\right)+\varepsilon^{\overline{\overline{s}}}\rho^{s}\mathbf{v}^{\overline{s}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\rho^{s}\mathbf{g}^{\overline{s}}-\varepsilon^{\overline{\overline{w}}}\rho^{w}\mathbf{g}^{\overline{w}}\\
&\quad-\eta^{\overline{\overline{w}}}\nabla\theta^{\overline{\overline{w}}}-\sum_{i\in\{A,B\}}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\nabla\left(\mu^{\overline{iw}}+\psi^{\overline{w}}\right)\\
&\quad-\hat{K}_{M}^{A}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{Aw}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{As}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathsf{C}^{s}}{3\rho^{s}j^{s}}+\psi^{\overline{s}}\right)\right]\left(\mathbf{v}_{s}^{\overline{ws}}+\mathbf{u}_{As}^{\overline{ws}}\right)\\
&\quad-\nabla\cdot\left[\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}-\varepsilon^{\overline{\overline{w}}}p^{w}\mathsf{I}+\varepsilon^{\overline{\overline{ws}}}\left(\mathsf{I}-\mathsf{G}^{ws}\right)\gamma^{ws}\right]-\hat{\mathsf{R}}^{w}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)=\mathbf{0}\,.
\end{aligned} \tag{10.85}$$

In the absence of mass exchange and when temperature is constant, these equations are identical to Eqs. (9.81)–(9.83) derived for the case of no mass exchange and no dispersion under isothermal conditions. For the case of slow flow where the inertial and mass exchange terms are small, the momentum equations can be simplified as in Sect. 9.7. The temperature variability in the current derivation enters the momentum equations because it impacts the elements of the chemical potential. It also influences the expressions for density and chemical potential through state equations.

Internal Energy Conservation for *w*, *ws*, and *s* Entities

Because entities may have different temperatures, energy equations may be written for each entity. Here, for exposition purposes, we will use the internal energy equation derived as Eq. (6.210). We will consider the case where terms in that equation that contain a velocity difference squared are considered to contribute negligibly to internal energy transport. Because $\overset{\kappa\to\alpha}{\mathbf{T}_0}$ is on the order of velocity from the closure relations of Eqs. (10.76) and (10.77) and it appears in Eq. (6.210) multiplying a velocity, that term is of order velocity squared and can be neglected. With these simplifications, Eq. (6.210) reduces to

$$\begin{aligned}
&\frac{\mathrm{D}^{\overline{\alpha}}E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+E^{\overline{\overline{\alpha}}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\sum_{i\in\mathfrak{J}_{s}}\overset{i\kappa\to i\alpha}{M}\,\overline{E}_{i}^{\overline{\overline{\alpha,\kappa}}}-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{Q_{1}}\\
&\quad-\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right)=0\quad\text{for }\alpha\in\mathfrak{J}\,.
\end{aligned} \tag{10.86}$$

Closure relations, in addition to those used for mass and momentum conservation, are Eqs. (10.74) and (10.75) for inter-entity energy exchanges and Eqs. (10.60), (10.61), and (10.64) for intra-entity non-advective heat transfer. For the *w*, *s*, and *ws* entities, the internal energy equations simplify, respectively, to

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{w}} E^{\overline{\overline{w}}}}{\mathrm{D}t} + E^{\overline{\overline{w}}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{w}}} + \hat{K}_M^A \left[\frac{1}{\theta^{\overline{\overline{w}}}} \left(\mu^{\overline{Aw}} + \psi^{\overline{w}} \right) - \frac{1}{\theta^{\overline{\overline{s}}}} \left(\mu^{\overline{As}} + \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^s}{3\rho^s j^s} + \psi^{\overline{s}} \right) \right] E_{Aw}^{\overline{ws}} \\
&\quad - p_w^{ws} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} - \hat{K}_E^w \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) + \varepsilon^{\overline{\overline{w}}} p^w \mathbf{l}{:}\mathbf{d}^{\overline{\overline{w}}} \\
&\quad + \nabla\cdot \left[\varepsilon^{\overline{\overline{w}}} \rho^w \omega^{A\overline{w}} (\overline{H}^{\overline{Aw}} - \overline{H}^{\overline{Bw}}) \mathbf{u}^{\overline{\overline{Aw}}} \right] + \nabla\cdot \left[\varepsilon^{\overline{\overline{w}}} \hat{\mathbf{k}}_{\theta}^{w} \cdot \nabla \left(\frac{1}{\theta^{\overline{\overline{w}}}} \right) \right] = 0 \,, \qquad (10.87)
\end{aligned}
$$

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{s}} E^{\overline{\overline{s}}}}{\mathrm{D}t} + E^{\overline{\overline{s}}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{s}}} - \hat{K}_M^A \left[\frac{1}{\theta^{\overline{\overline{w}}}} \left(\mu^{\overline{Aw}} + \psi^{\overline{w}} \right) - \frac{1}{\theta^{\overline{\overline{s}}}} \left(\mu^{\overline{As}} + \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^s}{3\rho^s j^s} + \psi^{\overline{s}} \right) \right] \overline{E}_{As}^{ws} \\
&\quad - \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} - \hat{K}_E^s \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) - \varepsilon^{\overline{\overline{s}}} \mathbf{t}^s{:}\mathbf{d}^{\overline{\overline{s}}} \\
&\quad + \nabla\cdot \left[\varepsilon^{\overline{\overline{s}}} \rho^s \omega^{A\overline{s}} (\overline{H}^{\overline{As}} - \overline{H}^{\overline{Cs}}) \mathbf{u}^{\overline{\overline{As}}} \right] + \nabla\cdot \left[\varepsilon^{\overline{\overline{s}}} \hat{\mathbf{k}}_{\theta}^{s} \cdot \nabla \left(\frac{1}{\theta^{\overline{\overline{s}}}} \right) \right] = 0 \,, \qquad (10.88)
\end{aligned}
$$

and

$$
\begin{aligned}
&\frac{\mathrm{D}^{\overline{ws}} E^{\overline{\overline{ws}}}}{\mathrm{D}t} + E^{\overline{\overline{ws}}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{ws}}} \\
&\quad - \hat{K}_M^A \left[\frac{1}{\theta^{\overline{\overline{w}}}} \left(\mu^{\overline{Aw}} + \psi^{\overline{w}} \right) - \frac{1}{\theta^{\overline{\overline{s}}}} \left(\mu^{\overline{As}} + \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^s}{3\rho^s j^s} + \psi^{\overline{s}} \right) \right] \left(E_{Aw}^{\overline{ws}} - E_{As}^{\overline{ws}} \right) \\
&\quad + p_w^{ws} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} + \hat{K}_E^w \left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) + \langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s \rangle_{\Omega_{ws},\Omega_{ws}} \frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{s}}}}{\mathrm{D}t} \\
&\quad + \hat{K}_E^s \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right) - \varepsilon^{\overline{\overline{ws}}} \gamma^{ws} \left(\mathbf{l} - \mathbf{G}^{ws} \right){:}\mathbf{d}^{\overline{\overline{ws}}} \\
&\quad + \nabla\cdot \left[\varepsilon^{\overline{\overline{ws}}} \hat{\mathbf{k}}_{\theta}^{ws} \cdot \nabla \left(\frac{1}{\theta^{\overline{\overline{ws}}}} \right) \right] = 0 \,. \qquad (10.89)
\end{aligned}
$$

Equations (10.79)–(10.89) are a set of closed conservation equations. We point out that this set has been obtained making use of a number of restrictions and approximations. The interface is massless. Only two chemical species are present in each phase; only one is exchanged between phases. Perhaps the most severe constraint is the omission of cross-coupling in the development of the expressions for non-advective heat and mass transport. Equations of state are needed. Coefficients that arise in the equations must be determined. The primary and secondary restrictions, the SEI approximations, and approximations made in linearizing the closure relations are all places where opportunities to make the model more general can be found. Despite the constraints applied, additional simplifications can still be employed and are often invoked (e.g., the inertial and mass exchange terms in the momentum equation are taken to be small, dispersion in the solid phase is considered negligible, the gradient in chemical potentials is expressed in terms of pressure and mass fraction gradients, and/or all properties of the *ws* interface are neglected). The utility of the TCAT approach is evident in the fact that all assumptions and approximations are explicit. Indeed, many assumptions that are intrinsic to porous medium heat and mass transport models become explicit.

10.11 Summary

In this chapter, we have illustrated the TCAT approach for deriving macroscale models for energy and species transport in a single-fluid-phase system. The CEI derived as Eq. (10.14) is of archival value. A general SEI has been obtained as Eq. (10.26) by applying SEI approximations. Secondary restrictions were then applied to obtain Eq. (10.33), a somewhat simplified but still rather general SEI that can be applied to obtain closure relations for the single-fluid-phase system. Special cases of this SEI are also obtained for restricted cases of energy and mass transfer culminating in a closed model. The need to have the same number of equations as unknowns was emphasized, and the challenges of meeting this requirement are alluded to. The advantages of TCAT in requiring that all approximations be explicit in model formulation can seem to be somewhat discouraging. However, one should understand that encountering the need for approximation in a complete theory is superior to ignorance of the fact that some hidden assumptions are implicitly included in a simple set of equations.

Systems that can be modeled based upon the compositional analysis done span a broad spectrum. As an example, the important case of a dilute system was considered. The SEI was used to posit closure relations for deviation velocities and inter-entity mass transfer. Reactions were considered and complicating factors discussed. For both reactions and mass transfer, multiscale modeling may be necessary in some instances.

The CEI and SEI’s derived in this chapter provide bases for considerable work building models. These models go well beyond the simple examples that were considered. For example, non-dilute systems, systems with different numbers of species, and systems in which fluxes depend upon not only their conjugate forces but also on other forces through Onsager-like cross coupling can be formulated based on the tools provided in this chapter. Significant extensions to the work presented here can be built on the bases of different approximations and different closure relations.

Exercises

10.1. Develop the closed conservation equations corresponding to the system described in Sect. 10.6.

10.2. Start with the SEI of Eq. (10.33).

a. Simplify this SEI for the case of non-isothermal, constant-composition flow with no interphase mass exchange.
b. Identify the number of unknowns that must be accounted for, the number of available equations, and the sources of additional equations needed to be able to close the system.
c. Determine the closed conservation equations needed to model the system.

10.3. Suppose the problem of interest is as described in Sect. 10.9. Assume that exchange of species A between the w and s phases is fast compared to other processes so that rather than being a kinetic process, it is an equilibrium process with $\omega^{A\overline{s}} = F(\omega^{A\overline{w}})$ where F is some function that describes the relation between the mass fractions of A in the two phases. Find the alteration to species mass conservation described by Eqs. (10.79)–(10.82) that models this system.

10.4. Show that instead of deleting the term involving $\nabla\theta^{\overline{\overline{w}}}$ from line 15 in Eq. (10.33) to obtain line 10 of Eq. (10.54), this term can be incorporated into the gradient of chemical potential taken holding temperature constant.

10.5. Start with the general SEI of Eq. (10.26). Assume the system is isothermal but that Secondary Restriction 10.3 does not apply. Assume that the w phase is composed of species A and B, the s phase is composed of species A and C, and the interface is composed only of species A. Allow for inter-entity mass transport of species A.

a. Make appropriate assumptions to obtain an SEI in force-flux form that is suitable for this system.
b. Ensure that the number of equations and unknowns match so that the equation system can be closed.
c. Obtain the closed conservation equations that can be used to model this system.

10.6. In Sect. 10.10.2, closure was obtained using the internal energy equation. As an alternative, the total energy equation can be used. Obtain the closed total energy equation and identify any assumptions that might be needed to ensure that they are interchangeable for modeling.

10.7. For the unithermal case, a single energy equation is needed to model the system. Provide this equation for the system described in Sect. 10.8.

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Chapter 11
Two-phase Flow

11.1 Overview

This chapter is the third that presents an example application of TCAT to a porous medium flow and transport problem. Single-phase flow was modeled in Chap. 9 . The analysis considered three entities: a fluid phase, *w*, a solid phase, *s*, and the interface between the phases, *ws*. In Chap. 10, the additional feature of chemical species transport was added to the analysis. In both chapters, the derivations began with general macroscale conservation, thermodynamic, and evolution equations and then proceeded to produce a closed set of conservation equations following the steps highlighted in Fig. 9.1. In fact, the derivations of the preceding chapters incorporate all the elements of macroscale TCAT analysis needed to formulate a closed larger-scale model. The purpose of the present chapter is to provide a TCAT analysis for two-fluid-phase flow in a porous medium. It follows the same procedures as the preceding two chapters, but it requires additional manipulations and an additional set of assumptions because the system is physically more complex.

The additional complexities stem from the more intricate morphology of the two-fluid porous medium system in comparison to the single-fluid case. The solid phase is denoted as the *s* phase, and *w* and *n* are used to identify the wetting and non-wetting fluid phases.[1] Although the combined volume fraction occupied by the fluid phases in the porous medium changes only very slowly, the volume fraction occupied by each fluid can change much more quickly. The volume fractions and their rates of change are important elements describing the fluid-phase behavior. The presence of three phases also means that three interface types are possible, denoted *wn*, *ws*, and *ns*. Thus, in contrast to the single-fluid system, a particular fluid may wet only a portion of the solid surface while the other fluid will be in contact

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[1] Although we use *w* and *n* as convenient symbols to designate which of the fluid phases preferentially wets the solid, cases exist where the solid does not have uniform properties and is preferentially wet by one fluid in one region and by the other fluid in a different region. This situation is called “mixed wettability.” Although we will not be explicitly considering this case here, one should realize that the use of *w* or *n* to designate the fluid phases need not indicate that a phase is always preferentially wetting.

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with the remaining fraction of the solid surface. Changes in the wetted fraction impact system behavior. Additionally, the *wn* interface between the two fluids is more dynamic than the solid surface. The *wn* interface deforms, grows, contracts, and transports through the system in ways and at rates that the solid-fluid interfaces do not. The processes of *wn* interface deformation and transport, as well as the jump in fluid pressure that can occur at this surface, play a very significant role in the behavior of the system. Lastly, the presence of three phases allows for the formation of a curve on the solid surface, designated as a *wns* common curve, where the three interface types meet. The displacement of this curve on the solid surface coincides with wetting or drying of the surface. The properties and dynamics of the common curve are of limited importance in comparison to the movement of the fluid phases and the fluid-fluid interface, but it provides an element of system dynamics that must, at least, be recognized.

Despite the additional elements of the two-fluid-phase system, the implementation of the TCAT approach in developing the equations shares the general approach of the last two chapters, particularly with Chap. 9 where species transport is not considered. We will take advantage of these similarities by borrowing elements of the previous derivations to reduce the work here. Nevertheless, in the end, the manipulations required to complete the particular derivation are more extensive than those shown previously. Most of the effort in this chapter is devoted to the elements of the derivation that are an extension to the single-fluid case.

The TCAT approach to obtaining two-fluid-phase flow equations illustrates explicitly the contributions that the *wn* interface and *wns* common curve make to the physics of the flow. True-to-mechanism models should include variables known to be important. These include interfacial and curvilinear tensions and curvatures, the contact angle between the fluid and solid phases, and specific interfacial areas and common curve lengths. None of these quantities appear explicitly in common multiphase flow models used in the petroleum industry or for environmental applications. Conversely, all of these quantities arise in a careful analysis of conditions that must hold at equilibrium in a two-fluid-phase porous medium system. Thus, it can be reasoned that the underlying physics of importance is being represented in common two-fluid-phase flow models implicitly through parameterization of hysteretic and non-linear closure relations that are used to produce closed models. The TCAT models formulated in this chapter include known mechanisms explicitly because they emerge naturally in the formulation. A comparison of these results with standard formulations provides insights into why multiphase models are so difficult to validate.

The sections that follow borrow from the derivations of the preceding two chapters. The derivation leads to a CEI that can serve as an entry point for derivation of a hierarchy of models based on approximate SEI's. An example of a closed model is provided, and the derivation will indicate how a more general model could be developed.

11.2 Primary Restrictions

The first set of primary restrictions to be applied is almost the same as Primary Restrictions 9.1–9.3 stated in Sect. 9.2. In fact, only the first of these three restrictions needs to be altered to take into account the additional entities. The three primary restrictions are stated here for convenience:

Primary Restriction 11.1 (System and Scale)
The system of concern consists of two fluid phases, w and n, a relatively immobile solid phase s, interfaces between each pair of phases denoted respectively as wn, ws, and ns, and a wns common curve where the three interfaces meet. The spatial scale of concern is the macroscale, ℓ^{ma}, with $\ell_{\text{r}}^{\text{r}} \ll \ell^{\text{ma}} \ll \ell^{\text{me}}$ where $\ell_{\text{r}}^{\text{r}}$ and ℓ^{me} are the resolution scale and megascale of the system, respectively.[2] *The domain of the system is Ω with boundary Γ.*

Primary Restriction 11.2 (Phenomena Modeled)
The phenomena of concern consist of the transport of mass, momentum, and energy in each of the entities. Transport phenomena of various chemical species within an entity will not be modeled explicitly.

Primary Restriction 11.3 (Thermodynamic Theory)
Classical irreversible thermodynamics (CIT) is employed to describe the thermodynamic behavior of the system entities at equilibrium and near-equilibrium states. The solid phase is modeled as elastic.

We propose one additional primary restriction that is appropriate for modeling a solid phase that deforms negligibly at a small scale when subjected to the forces exerted on it, particularly by the common curve. This restriction states that the surface of the solid material at the microscale has a unique normal vector at every point.

Primary Restriction 11.4 (Smooth Solid Surface)
From a microscale perspective, the outward unit normal vector at each point on the solid surface, $\mathbf{n}_s$, is unique.

No similar restriction applies to the fluid phases that contact the solid because the fluid-fluid interface may meet the solid surface at a non-zero contact angle.

We emphasize that we are employing TCAT at the macroscale such that all equations have been averaged from the microscale to this larger scale. At this larger scale, the behavior of the entities and their properties are modeled three-dimensionally per unit of averaging volume regardless of whether they apply to one-, two-, or three-dimensional microscale domains. The presumed separation of length scales means that macroscale variables and parameters will be well-defined. We have chosen to exclude species transport from the model in the interest of simplicity. Chap. 10 shows how species transport can be included in a single-fluid-phase model if desired. An analogous approach can be employed for the two-fluid-phase model. The

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[2] The descriptions of length scales are provided in the discussion of Eq. (1.1).

addition of the third phase means that we will include conservation and thermodynamic equations for the common curve, which did not arise in the earlier derivations. Additionally, the ability of a solid phase to sustain a singularity, a concentrated force, at a common curve will be included.

11.3 Constrained Entropy Inequality Statement

The development of the CEI for the two-fluid-phase system follows the same steps as in Sect. 9.4. Because of the similarity of the early steps of the derivation of the CEI in that previous case and the present case, these steps will be merely outlined here with further detail available in Chap. 9. Some algebraic manipulations involving rearrangements leading to the CEI, similar to those in Chap. 9, are relegated to Sect. C.3 to avoid distraction from the goal of obtaining closed equations. The derivation follows the general TCAT steps highlighted in Fig. 9.1.

11.3.1 Entropy Inequality

The entropy inequality may be written directly from the next to the last row of Table 6.3 according to Eq. (9.5) as

$$\sum_{\alpha\in\mathcal{J}} \mathcal{S}_*^{\overline{\overline{\alpha}}} = \sum_{\alpha\in\mathcal{J}} \Lambda^{\overline{\overline{\alpha}}} > 0 \,, \tag{11.1}$$

where, for the present problem, $\mathcal{J}$ is the index set for the three phases, three interfaces, and the common curve,

$$\mathcal{J} = \{w, n, s, wn, ws, ns, wns\} \,. \tag{11.2}$$

11.3.2 Augmented Entropy Inequality

The augmented entropy inequality is obtained as Eq. (9.20), which states

$$\begin{aligned}\sum_{\alpha\in\mathcal{J}} \mathcal{S}_*^{\overline{\overline{\alpha}}} + \sum_{\alpha\in\mathcal{J}} \lambda_{\mathcal{E}}^{\alpha} \mathcal{E}_*^{\overline{\overline{\alpha}}} + \sum_{\alpha\in\mathcal{J}} \boldsymbol{\lambda}_{\boldsymbol{\mathcal{P}}}^{\alpha} \cdot \boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}} + \sum_{\alpha\in\mathcal{J}} \lambda_{\mathcal{M}}^{\alpha} \mathcal{M}_*^{\overline{\overline{\alpha}}} + \sum_{\alpha\in\mathcal{J}} \lambda_{\mathcal{G}}^{\alpha} \mathcal{G}_*^{\overline{\overline{\alpha}}} \\ + \sum_{\alpha\in\mathcal{J}} \lambda_{\mathcal{T}}^{\alpha} \mathcal{T}_*^{\overline{\overline{\alpha}}} + \sum_{\alpha\in\mathcal{J}} \lambda_{\mathcal{T}\mathcal{G}}^{\alpha} \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}} = \sum_{\alpha\in\mathcal{J}} \Lambda^{\overline{\overline{\alpha}}} \geq 0 \,,\end{aligned} \tag{11.3}$$

where the conservation and balance equations $\mathcal{S}_*^{\overline{\overline{\alpha}}}$, $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, $\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$, $\mathcal{M}_*^{\overline{\overline{\alpha}}}$, and $\mathcal{G}_*^{\overline{\overline{\alpha}}}$ are available in Table 6.3 and the equation numbers for the thermodynamic relations $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$ are given in Table 7.2.

11.3.3 Selection of Lagrange Multipliers

The Lagrange multipliers, the λ and $\boldsymbol{\lambda}$ coefficients in Eq. (11.3), are solved for as in Sect. 9.4.2. They are selected with the goal of eliminating time derivatives from the formulation as possible. The resulting values are identical to Eqs. (9.25)–(9.30). As a consequence, the augmented entropy inequality has the same form as Eq. (9.31) but makes use of the expanded index set of entities as listed in Eq. (11.2). This AEI

$$\begin{aligned}\sum_{\alpha\in\mathfrak{J}} \mathcal{S}_*^{\overline{\overline{\alpha}}} - \sum_{\alpha\in\mathfrak{J}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathcal{E}_*^{\overline{\overline{\alpha}}} + \sum_{\alpha\in\mathfrak{J}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathbf{v}^{\overline{\alpha}}\cdot\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}} \\ + \sum_{\alpha\in\mathfrak{J}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}} - \frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2} + K_E^{\overline{\overline{\alpha}}}\right)\mathcal{M}_*^{\overline{\overline{\alpha}}} \\ - \sum_{\alpha\in\mathfrak{J}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathcal{G}_*^{\overline{\overline{\alpha}}} + \sum_{\alpha\in\mathfrak{J}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathcal{T}_*^{\overline{\overline{\alpha}}} + \sum_{\alpha\in\mathfrak{J}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}} = \sum_{\alpha\in\mathfrak{J}} \Lambda^{\overline{\overline{\alpha}}} \geq 0\,. \qquad (11.4)\end{aligned}$$

11.3.4 Expanded CEI

Inserting the forms of each of the conservation and thermodynamic equations into Eq. (11.4) and eliminating the time derivatives that cancel yields an equation similar to Eq. (9.32). However, this expanded equation is much longer because it describes entropy generation for a seven-entity system rather than a three-entity system. This equation is an important starting point for rearrangement of the AEI to obtain the CEI. It is provided as Eq. (C.82) of Appendix C, expanded out with the time derivatives eliminated. The terms in the equation are kept in the same order as in their precursor conservation and thermodynamic equations, except concentrated source terms are combined for convenience. Thus, difficulty in constructing this expanded equation is minimized. However, lengthy mathematical manipulations are required to arrange this equation into the CEI form consisting of products of macroscale forces and fluxes, as possible. No approximations are made, but the regrouping of terms is extensive. Guidance to successful completion of the formulation is provided in Sect. C.3. Here, in the main body of the text, we provide the result of substituting the designated equations into Eq. (11.4) to obtain Eq. (C.82). After collecting terms, we obtain the following CEI:

$$
\begin{aligned}
&- \sum_{\alpha \in \mathfrak{I}_{\mathrm{P}}} \left\{ \varepsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left[\varepsilon^{\overline{\overline{\alpha}}} h^{\alpha} + \left\langle \eta_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \right.\right. \\
&\qquad \left.\left. + \left\langle \rho_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{\alpha} + \psi_{\alpha} - \mu^{\overline{\alpha}} - K_E^{\overline{\overline{\alpha}}} - \psi^{\overline{\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \right] \right\} \\
&- \sum_{\alpha \in \mathfrak{I}_{\mathrm{I}}} \left\{ \varepsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left[\varepsilon^{\overline{\overline{\alpha}}} h^{\alpha} + \left\langle \eta_{\alpha} \frac{\mathrm{D}'^{\overline{s}} \left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \right.\right. \\
&\qquad \left.\left. + \left\langle \rho_{\alpha} \frac{\mathrm{D}'^{\overline{s}} \left(\mu_{\alpha} + \psi_{\alpha} - \mu^{\overline{\alpha}} - K_E^{\overline{\overline{\alpha}}} - \psi^{\overline{\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \right] \right\} \\
&- \left\{ \varepsilon^{\overline{\overline{wns}}} b^{wns} - \frac{1}{\theta^{\overline{\overline{wns}}}} \left[\varepsilon^{\overline{\overline{wns}}} h^{wns} + \left\langle \eta_{wns} \frac{\mathrm{D}''^{\overline{s}} \left(\theta_{wns} - \theta^{\overline{\overline{wns}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wns},\Omega} \right.\right. \\
&\qquad \left.\left. + \left\langle \rho_{wns} \frac{\mathrm{D}''^{\overline{s}} \left(\mu_{wns} + \psi_{wns} - \mu^{\overline{wns}} - K_E^{\overline{\overline{wns}}} - \psi^{\overline{wns}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wns},\Omega} \right] \right\} \\
&- \sum_{\alpha \in \mathfrak{I}_{/S}} \nabla \cdot \left[\varepsilon^{\overline{\overline{\alpha}}} \boldsymbol{\varphi}^{\overline{\overline{\alpha}}} - \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}} \right) \right] \\
&- \nabla \cdot \left\{ \varepsilon^{\overline{\overline{s}}} \boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{s}}}} \left[\varepsilon^{\overline{\overline{s}}} \mathbf{q}^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{s}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{s}}} - \left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s,\Omega} \right] \right\} \\
&+ \sum_{\alpha \in \mathfrak{I}_{\mathrm{f}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} p^{\alpha} \mathbf{I} \right) {:} \mathbf{d}^{\overline{\overline{\alpha}}} + \frac{1}{\theta^{\overline{\overline{s}}}} \left(\varepsilon^{\overline{\overline{s}}} \mathbf{t}^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{s}}} \mathbf{t}^{s} \right) {:} \mathbf{d}^{\overline{\overline{s}}} \\
&+ \sum_{\alpha \in \mathfrak{I}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left[\varepsilon^{\overline{\overline{\alpha}}} \mathbf{t}^{\overline{\overline{\alpha}}} - \left\langle \mathbf{I}'_{\alpha} \gamma_{\alpha} \right\rangle_{\Omega_{\alpha},\Omega} \right] {:} \mathbf{d}^{\overline{\overline{\alpha}}} \\
&+ \frac{1}{\theta^{\overline{\overline{wns}}}} \left[\varepsilon^{\overline{\overline{wns}}} \mathbf{t}^{\overline{\overline{wns}}} + \left\langle \mathbf{I}''_{wns} \gamma_{wns} \right\rangle_{\Omega_{wns},\Omega} \right] {:} \mathbf{d}^{\overline{\overline{wns}}} \\
&- \sum_{\alpha \in \mathfrak{I}_{/S}} \left(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}} \right) \cdot \nabla \left(\frac{1}{\theta^{\overline{\overline{\alpha}}}} \right) \\
&- \left[\varepsilon^{\overline{\overline{s}}} \mathbf{q}^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{s}}} \mathbf{q}_{\mathbf{g}}^{\overline{\overline{s}}} - \left\langle \left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{j_s} \mathbf{I} \right) \cdot \left(\mathbf{v}_s - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_s,\Omega} \right] \cdot \nabla \left(\frac{1}{\theta^{\overline{\overline{s}}}} \right) \\
&+ \sum_{\alpha \in \mathfrak{I}_{\mathrm{f}}} \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\alpha}} \overset{\alpha \to \kappa}{M} \left[\frac{1}{\theta^{\overline{\overline{\alpha}}}} \left(\mu^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}} \right) - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \left(\mu^{\overline{\kappa}} + K_E^{\overline{\overline{\kappa}}} + \psi^{\overline{\kappa}} \right) \right] \\
&+ \sum_{\kappa \in \mathfrak{I}_{\mathrm{cs}}} \overset{s \to \kappa}{M} \left[\frac{1}{\theta^{\overline{\overline{s}}}} \left(\mu^{\overline{s}} + K_E^{\overline{\overline{s}}} + \psi^{\overline{s}} + \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^{s}}{3 \rho^{s} j^{s}} \right) - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \left(\mu^{\overline{\kappa}} + K_E^{\overline{\overline{\kappa}}} + \psi^{\overline{\kappa}} \right) \right]
\end{aligned}
$$

$$+\sum_{\kappa\in\mathfrak{J}_{\mathrm{cs}}}\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\rho_s j_s}-\frac{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s}{\rho_s}-\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^s}{3\rho^s j^s}\right)\rho_s\left(\mathbf{v}_s-\mathbf{v}_\kappa\right)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}$$ 16

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\overset{\alpha\to wns}{M}\left[\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)-\frac{1}{\theta^{\overline{\overline{wns}}}}\left(\mu^{\overline{wns}}+K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\right]$$ 17

$$-\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\left\{\overset{\alpha\to\kappa}{Q}+\overset{\alpha\to\kappa}{G}+\left(\overline{E}_\alpha^{\overline{\kappa}}+K_{E\alpha}^{\overline{\overline{\kappa}}}+\psi_\alpha^{\overline{\kappa}}\right)\overset{\alpha\to\kappa}{M}\right.$$ 18

$$+\left[\overset{\alpha\to\kappa}{\mathbf{T}}+\frac{\left(\mathbf{v}_\alpha^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{\alpha\to\kappa}{M}\right]\cdot\left(\mathbf{v}_\alpha^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)$$ 19

$$\left.-\left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)p_\alpha\right\rangle_{\Omega_\kappa,\Omega}\right\}\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)$$ 20

$$-\sum_{\kappa\in\mathfrak{J}_{\mathrm{cs}}}\left\{\overset{s\to\kappa}{Q}+\overset{s\to\kappa}{G}+\left(\overline{E}_s^{\overline{\kappa}}+K_{Es}^{\overline{\overline{\kappa}}}+\psi_s^{\overline{\kappa}}\right)\overset{s\to\kappa}{M}\right.$$ 21

$$+\left[\overset{s\to\kappa}{\mathbf{T}}+\frac{\left(\mathbf{v}_s^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{s\to\kappa}{M}\right]\cdot\left(\mathbf{v}_s^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)$$ 22

$$\left.+\left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}}\right)\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}\right\}\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)$$ 23

$$-\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\left\{\overset{\alpha\to wns}{Q}+\overset{\alpha\to wns}{G}+\left(\overline{E}_\alpha^{\overline{wns}}+K_{E\alpha}^{\overline{\overline{wns}}}+\psi_\alpha^{\overline{wns}}\right)\overset{\alpha\to wns}{M}\right.$$ 24

$$+\left[\overset{\alpha\to wns}{\mathbf{T}}+\frac{\left(\mathbf{v}_\alpha^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{\alpha\to wns}{M}\right]\cdot\left(\mathbf{v}_\alpha^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)$$ 25

$$\left.+\left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha\right\rangle_{\Omega_{wns},\Omega}\right\}\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)$$ 26

$$+\left[\overset{wns\to s}{Q^*}+\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\left(\mathbf{v}_s^{\overline{wns}}-\mathbf{v}_s\right)\right\rangle_{\Omega_{wns},\Omega}\right.$$ 27

$$\left.+\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\left(\mathbf{v}_s-\mathbf{v}_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\right]\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)$$ 28

$$-\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\eta^{\overline{\overline{\alpha}}}\nabla\theta^{\overline{\overline{\alpha}}}-\nabla\left(\varepsilon^{\overline{\overline{\alpha}}}p^\alpha\right)+\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\nabla\left(\mu^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)+\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\mathbf{g}^{\overline{\alpha}}\right.$$ 29

$$\left.-\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}^-}\left[\overset{\alpha\to\kappa}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{\alpha\to\kappa}{M}+\left(\mathbf{v}_\alpha^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)\overset{\alpha\to\kappa}{M}\right]\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)$$ 30

$$-\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\eta^{\overline{\overline{\alpha}}}\nabla\theta^{\overline{\overline{\alpha}}}+\nabla\cdot\left\langle\mathsf{I}'_\alpha\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}+\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\nabla\left(\mu^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\right.$$ 31

$$+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}+\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\left[\overset{\kappa\to\alpha}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{\kappa\to\alpha}{M}+\left(\mathbf{v}_{\kappa}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\overset{\kappa\to\alpha}{M}\right] \tag{32}$$

$$-\left[\overset{\alpha\to wns}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{\alpha\to wns}{M}+\left(\mathbf{v}_{\alpha}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\overset{\alpha\to wns}{M}\right] \tag{33}$$

$$-\left\langle\eta_{\alpha}\left(\mathsf{I}-\mathsf{I}'_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}} \tag{34}$$

$$\left.-\left\langle\rho_{\alpha}\left(\mathsf{I}-\mathsf{I}'_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\left(\mu^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right) \tag{35}$$

$$-\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left\{\eta^{\overline{\overline{wns}}}\nabla\theta^{\overline{\overline{\overline{wns}}}}-\nabla\cdot\left\langle\mathsf{I}''_{wns}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\right. \tag{36}$$

$$+\varepsilon^{\overline{\overline{wns}}}\rho^{wns}\nabla\left(\mu^{\overline{wns}}+K_{E}^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)+\varepsilon^{\overline{\overline{wns}}}\rho^{wns}\mathbf{g}^{\overline{wns}} \tag{37}$$

$$+\sum_{\kappa\in\mathfrak{I}_{\mathrm{cwns}}^{+}}\left[\overset{\kappa\to wns}{\mathbf{T}}-\frac{\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{\kappa\to wns}{M}+\left(\mathbf{v}_{\kappa}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\overset{\kappa\to wns}{M}\right] \tag{38}$$

$$-\left\langle\eta_{wns}\left(\mathsf{I}-\mathsf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\theta^{\overline{\overline{\overline{wns}}}} \tag{39}$$

$$-\left\langle\rho_{wns}\left(\mathsf{I}-\mathsf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\left(\mu^{\overline{wns}}+K_{E}^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right) \tag{40}$$

$$\left.-\left\langle\mathbf{t}_{s}^{*}\cdot\mathbf{n}_{s}\right\rangle_{\Omega_{wns},\Omega}\right\}\cdot\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right) \tag{41}$$

$$+\frac{1}{\theta^{\overline{\overline{wn}}}}\left\langle\left[p_{w}\mathbf{n}_{w}+p_{n}\mathbf{n}_{n}+\gamma_{wn}\left(\nabla'\cdot\mathsf{I}'_{wn}\right)\right.\right. \tag{42}$$

$$\left.\left.+\rho_{wn}\mathbf{g}_{wn}\cdot\left(\mathsf{I}-\mathsf{I}'_{wn}\right)\right]\cdot\left(\mathbf{v}_{wn}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega} \tag{43}$$

$$+\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle\left[p_{w}\mathbf{n}_{w}-\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\mathbf{n}_{s}+\gamma_{ws}\left(\nabla'\cdot\mathsf{I}'_{ws}\right)\right.\right. \tag{44}$$

$$\left.\left.+\rho_{ws}\mathbf{g}_{ws}\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right]\cdot\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega} \tag{45}$$

$$+\frac{1}{\theta^{\overline{\overline{ns}}}}\left\langle\left[p_{n}\mathbf{n}_{n}-\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\mathbf{n}_{s}+\gamma_{ns}\left(\nabla'\cdot\mathsf{I}'_{ns}\right)\right.\right. \tag{46}$$

$$\left.\left.+\rho_{ns}\mathbf{g}_{ns}\cdot\left(\mathsf{I}-\mathsf{I}'_{ns}\right)\right]\cdot\left(\mathbf{v}_{ns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ns},\Omega} \tag{47}$$

$$-\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left\langle\left[\gamma_{wn}\mathbf{n}_{wn}+\gamma_{ws}\mathbf{n}_{ws}+\gamma_{ns}\mathbf{n}_{ns}+\gamma_{wns}\left(\nabla''\cdot\mathsf{I}''_{wns}\right)\right.\right. \tag{48}$$

$$\left.\left.-\rho_{wns}\mathbf{g}_{wns}\cdot\left(\mathsf{I}-\mathsf{I}''_{wns}\right)+\mathbf{n}_{s}\cdot\mathbf{t}_{s}^{*}\right]\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega} \tag{49}$$

$$
\begin{aligned}
&+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot(\mathbf{v}_s-\mathbf{v}_{wns})\,\frac{\boldsymbol{\sigma}_s^{*}:\mathbf{C}_s}{j_s}\right\rangle_{\Omega_{wns},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s^{*}\cdot(\mathbf{v}_s-\mathbf{v}_{wns})\right\rangle_{\Omega_{wns},\Omega}\\
&-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'_{ws}\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ws},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'_{ns}\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{ns},\Omega}\\
&+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\nabla\cdot\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\\
&+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\eta_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}}\\
&+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\\
&+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\left(\mu^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)\\
&+\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\eta_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\theta^{\overline{\overline{wns}}}\\
&-\frac{1}{\theta^{\overline{\overline{wns}}}}\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\\
&+\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle\rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\left(\mu^{\overline{wns}}+K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\\
&=\sum_{\alpha\in\mathfrak{J}}\Lambda^{\overline{\overline{\alpha}}}\ge 0\,.
\end{aligned}
\tag{11.5}
$$

This archival CEI can be used to derive a hierarchy of closed models of varying sophistication. Accomplishing this objective requires reducing the CEI to a strict macroscale force-flux form, the SEI. In the next section, an example of an SEI is presented.

11.4 Simplified Entropy Inequality

Reduction of Equation (11.5) to a strict macroscale force-flux form is necessary for it to guide the formulation of closure relations for two-fluid-phase-flow models. This reduction follows along the lines of the derivations in the preceding two chapters. It is important to recognize that, although the CEI given by Eq. (11.5) is unique for the two-fluid-phase system, the SEI approximations employed are not unique. The SEI approximations specify the manner in which groupings of terms are evaluated approximately. A range of alternative approximations exists for reducing the CEI to various macroscale force-flux forms. With the approximations listed explicitly, one can assess the appropriateness of the SEI for a problem of interest. Should some assumptions be deemed inappropriate in hindsight, one needs only to return to the

CEI as a starting point for developing a different SEI. Thus the CEI and the SEI are useful entry points in the analysis of two-phase flow.

The approach employed in deriving an SEI from Eq. (11.5) is similar to that used for single-phase flow in deriving Eq. (9.62) from Eq. (9.43). However, the SEI approximations needed are more extensive to account for the presence of the additional phase, interfaces, and common curve. A selection of reasonable SEI approximations will be detailed.

11.4.1 Required SEI Approximations

Table C.1 indicates that the set of forces identified to this point for the force-flux analysis is the set $\mathcal{V}_F$, where

$$\begin{aligned}\mathcal{V}_F = \Bigg\{ & \mathbf{d}^{\overline{\alpha}}, \nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right), \frac{1}{\theta^{\overline{\overline{\beta}}}}\left(\mu^{\overline{\beta}} + K_E^{\overline{\overline{\beta}}} + \psi^{\overline{\beta}}\right) - \frac{1}{\theta^{\overline{\overline{\gamma}}}}\left(\mu^{\overline{\gamma}} + K_E^{\overline{\overline{\gamma}}} + \psi^{\overline{\beta}}\right), \\ & \frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{s}} + K_E^{\overline{\overline{s}}} + \psi^{\overline{s}} + \frac{\sigma^{\overline{\overline{s}}}:\mathbf{C}^s}{3\rho^s j^s}\right) - \frac{1}{\theta^{\overline{\overline{\varepsilon}}}}\left(\mu^{\overline{\varepsilon}} + K_E^{\overline{\overline{\varepsilon}}} + \psi^{\overline{\varepsilon}}\right), \\ & \frac{1}{\theta^{\overline{\overline{\alpha}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}}, \frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}}, \mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \Bigg\} \\ & \text{for } \alpha \in \mathcal{J}, \kappa \in \mathcal{J}^-_{\mathrm{c}\alpha}, \beta \in \mathcal{J}_{/S}, \gamma \in \mathcal{J}^-_{\mathrm{c}\beta}, \varepsilon \in \mathcal{J}^-_{\mathrm{c}s} \, .\end{aligned} \tag{11.6}$$

Examination of Eq. (11.5) in light of this list of forces suggests that lines 1–8, 16, and 42–59 require attention to obtain a force-flux form. Essentially, these lines must be eliminated or approximated. The SEI approximations proposed can be divided into two classes for ease of presentation. The first set consists of basic SEI approximations that apply to lines 1–8 and 50–58. These are basic because they do not rely on any complex approximations to develop their form, and these approximations result in the elimination of lines 1–8 and 51–58 from the CEI. As a collateral effect, they also result in simplification of some of the other lines in the SEI. The second set is referred to as complex SEI approximations. These are needed to rearrange lines 42–50, terms that describe interactions among entities at entity boundaries. Complex SEI approximations allow breaking the products that appear in these lines in light of evolution considerations from Chap. 8. This breaking of products provides macroscale force-flux pairs, sometimes in conjunction with other lines of the SEI. These two types of SEI approximations will be treated in the following subsections.

11.4.2 Basic SEI Approximations

The approximations in this section eliminate some lines and terms in the CEI as a step to formation of the SEI. As a consequence of the SEI approximations, some terms are set to zero. More precisely, these terms are considered to be negligible relative to other terms in the SEI and are eliminated from consideration on that basis.

Lines 1–8

The first SEI approximation to be applied here is similar to that invoked for the single-phase-flow case in SEI Approximation 9.1. It addresses the terms in lines 1–8 of Eq. (11.5) and is stated:

SEI Approximation 11.1 (Macroscopically Simple System)
The system of concern is macroscopically simple, with the entropy source balanced by the sum of a heat source and deviation terms such that

$$\begin{aligned}\varepsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \frac{1}{\theta^{\overline{\overline{\alpha}}}} \Bigg[\varepsilon^{\overline{\overline{\alpha}}} h^{\alpha} &+ \left\langle \eta_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \\ &+ \left\langle \rho_{\alpha} \frac{\mathrm{D}^{\overline{s}} \left(\mu_{\alpha} + \psi_{\alpha} - \mu^{\overline{\alpha}} - K_E^{\overline{\overline{\alpha}}} - \psi^{\overline{\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \Bigg] = 0 \quad \textit{for } \alpha \in \mathfrak{J}_{\mathrm{P}} \,, \end{aligned} \tag{11.7}$$

$$\begin{aligned}\varepsilon^{\overline{\overline{\alpha}}} b^{\alpha} - \frac{1}{\theta^{\overline{\overline{\alpha}}}} \Bigg[\varepsilon^{\overline{\overline{\alpha}}} h^{\alpha} &+ \left\langle \eta_{\alpha} \frac{\mathrm{D}'^{\overline{s}} \left(\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \\ &+ \left\langle \rho_{\alpha} \frac{\mathrm{D}'^{\overline{s}} \left(\mu_{\alpha} + \psi_{\alpha} - \mu^{\overline{\alpha}} - K_E^{\overline{\overline{\alpha}}} - \psi^{\overline{\alpha}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{\alpha},\Omega} \Bigg] = 0 \quad \textit{for } \alpha \in \mathfrak{J}_{\mathrm{I}} \,, \end{aligned} \tag{11.8}$$

and

$$\begin{aligned}\varepsilon^{\overline{\overline{wns}}} b^{wns} - \frac{1}{\theta^{\overline{\overline{wns}}}} \Bigg[\varepsilon^{\overline{\overline{wns}}} h^{wns} &+ \left\langle \eta_{wns} \frac{\mathrm{D}''^{\overline{s}} \left(\theta_{wns} - \theta^{\overline{\overline{wns}}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wns},\Omega} \\ &+ \left\langle \rho_{wns} \frac{\mathrm{D}''^{\overline{s}} \left(\mu_{wns} + \psi_{wns} - \mu^{\overline{wns}} - K_E^{\overline{\overline{wns}}} - \psi^{\overline{wns}} \right)}{\mathrm{D}t} \right\rangle_{\Omega_{wns},\Omega} \Bigg] = 0 \,; \end{aligned} \tag{11.9}$$

and the entropy flux is balanced by a non-advective energy flux for all entities, consisting of heat and mechanical contributions, such that

$$\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}} - \frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}} + \varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}\right) = \mathbf{0} \quad \textit{for } \alpha \in \mathfrak{I}_{/S} \tag{11.10}$$

and

$$\varepsilon^{\overline{\overline{s}}}\boldsymbol{\varphi}^{\overline{\overline{s}}} - \frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left[\varepsilon^{\overline{\overline{s}}}\mathbf{q}^{\overline{\overline{s}}} + \varepsilon^{\overline{\overline{s}}}\mathbf{q}_{\mathbf{g}}^{\overline{\overline{s}}} - \left\langle\left(\mathbf{t}_s - \frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right] = \mathbf{0}\,. \tag{11.11}$$

By pairing the entropy and heat sources, and also dissipative entropy and heat fluxes, SEI Approximation 11.1 eliminates the first eight lines in Eq. (11.5).

Lines 13 and 52–58

The next SEI approximation addresses lines 13 and 52–58 of the CEI. Each of these lines involves the average of a product of terms wherein one factor is of the form $\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}$, and the averaging is over Ω_α. Thus breaking of products will lead to one of the factors being the average of a velocity difference that is zero. For example, if we make the approximation

$$\left\langle f_\alpha(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right\rangle_{\Omega_\alpha,\Omega} = \left\langle\frac{f_\alpha}{\rho_\alpha}\right\rangle_{\Omega_\alpha,\Omega_\alpha}\left\langle\rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}})\right\rangle_{\Omega_\alpha,\Omega}, \tag{11.12}$$

the second factor on the right side is zero based on the definition of density-weighted average velocity. For this reason, we expect terms of a similar form to the left side of Eq. (11.12), individually and collectively, to be small. We thus invoke an SEI approximation:

SEI Approximation 11.2 (Entity Velocity Deviations)
Expressions that involve the average over Ω_α, the domain of entity α, of a product of a microscale quantity with $\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}$ are assumed to be negligible.

This approximation eliminates part of line 13 and all of lines 52–58 of Eq. (11.5) from further consideration.

Lines 27, 28, 41, 49, and 50

We have allowed a concentrated non-advective solid stress (i.e., $\mathbf{t}_s^*$) to act at the common curve on a smooth solid surface. The only part of the concentrated stress tensor that appears is the vector $\mathbf{n}_s\cdot\mathbf{t}_s^*$. We note from condition Eq. (4.101) that the shear components at equilibrium satisfy the condition $\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{l}'_{ss} = 0$. We will assume that this component is negligible away from equilibrium and thus propose:

SEI Approximation 11.3 (Concentrated Stress Constraint)
The concentrated stress expressing interaction between the solid phase and the common curve satisfies the condition

$$\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{l}'_{ss} = \mathbf{0}' \quad \mathit{for}\ \mathbf{x} \in \Omega_{wns}\ , \tag{11.13}$$

even when the system is not at equilibrium. Therefore, the concentrated stress is given by

$$\mathbf{n}_s\cdot\mathbf{t}_s^* = \mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s\mathbf{n}_s \quad \mathit{for}\ \mathbf{x} \in \Omega_{wns}\ . \tag{11.14}$$

Equation (11.14) that arises from this SEI approximation may be substituted into lines 27, 28, 41, 49 and 50 of Eq. (11.5).

After this substitution into line 50, we see that both averages in this line involve a velocity difference, $\mathbf{n}_s\cdot(\mathbf{v}_s - \mathbf{v}_{wns})$. This quantity will be non-zero only if there is direct mass exchange between the solid surface and the common curve. Such an exchange requires mass flow from the solid to a common curve, essentially across an area of zero width. This would require a concentrated flow, a phenomenon that we have excluded in the formulation of the equations. Thus no direct mass exchange between the solid surface and the common curve is allowed. In addition, we will assume that the difference between the microscale solid-phase velocity averaged over the common curve and the solid-phase velocity averaged over the solid domain multiplied by the concentrated stress is of higher order smallness. These two conditions suggest the following SEI approximation:

SEI Approximation 11.4 (Solid-Common Curve Velocities)
No direct mass exchange between the solid phase and the common curve is modeled by the condition

$$\mathbf{n}_s\cdot(\mathbf{v}_s - \mathbf{v}_{wns}) = 0 \quad \mathit{for}\ \mathbf{x} \in \Omega_{wns}\ ; \tag{11.15}$$

and the concentrated stress multiplied by the unit normal $\mathbf{n}_s$ *dotted with the difference between the solid velocity averaged over the common curve and the microscale solid velocity averaged over the common curve is negligible such that*

$$\left\langle \mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s\mathbf{n}_s\cdot\left(\mathbf{v}_s^{\overline{wns}} - \mathbf{v}_s\right)\right\rangle_{\Omega_{wns},\Omega} = 0\ . \tag{11.16}$$

As a consequence of SEI Approximations 11.3 and 11.4, the velocity terms in lines 27 and 28 as well as all of line 50 of the CEI of Eq. (11.5) can be deleted.

Line 51

Equation (4.54) indicates that the microscopic shear stress, $\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ss}$, is zero at every point on the solid surface at equilibrium. If we consider both this stress and the difference between $\mathbf{v}_s$ and $\mathbf{v}^{\overline{s}}$ on the solid surface to be small away from equilibrium, the product of these quantities is of higher order smallness. This is a typical situation. Thus, we propose:

SEI Approximation 11.5 (Solid-phase Surface Stress)
The stress at the surface of the solid phase given by $\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws}$ *for* $\mathbf{x} \in \Omega_{ws}$ *and*

$\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{l}'_{ns}$ for $\mathbf{x} \in \Omega_{ns}$ is small, as is the difference between the solid-surface velocity and the average solid-phase velocity, such that the average of their product can be considered negligible with

$$\left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{l}'_{ws} \cdot \left(\mathbf{v}_s - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{ws},\Omega} = 0 \tag{11.17}$$

and

$$\left\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{l}'_{ns} \cdot \left(\mathbf{v}_s - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{ns},\Omega} = 0 \, . \tag{11.18}$$

As a consequence of SEI Approximation 11.5 both terms in line 51 of Eq. (11.5) are eliminated.

Line 16

Another approximation that we propose here relates to line 16 of the CEI that deals with the exchange of mass between the *s* phase and the *ws* and *ns* interfaces. Recall the microscale equilibrium condition Eq. (4.96), which states

$$\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s - \frac{2\boldsymbol{\sigma}_s : \mathbf{C}_s}{3 j_s} = 0 \quad \text{for } \mathbf{x} \in \Omega_{ws}, \Omega_{ns} \, . \tag{11.19}$$

Thus, line 16 contains a term that is approximately the average over the solid surface of the deviation of $\boldsymbol{\sigma}_s : \mathbf{C}_s / (3 \rho_s j_s)$ from its intrinsic average multiplied by the rate of mass exchange between the solid and the bounding surface. We consider this term to be negligible such that the following approximation holds:

SEI Approximation 11.6 (Solid Stress and Mass Exchange)
The average of the deviation of the solid surface stress from its average in the solid phase multiplied by the mass exchange rate is negligible such that

$$\left\langle \left(\frac{\boldsymbol{\sigma}_s : \mathbf{C}_s}{\rho_s j_s} - \frac{\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s}{\rho_s} - \frac{\boldsymbol{\sigma}^{\bar{\bar{s}}} : \mathbf{C}^s}{3 \rho^s j^s} \right) \rho_s \left(\mathbf{v}_s - \mathbf{v}_\kappa \right) \cdot \mathbf{n}_s \right\rangle_{\Omega_\kappa,\Omega} = 0 \quad \textit{for } \kappa \in \mathfrak{I}_{\mathrm{cs}} \, . \tag{11.20}$$

This approximation is exact when there is no mass exchange occurring at the solid surface. We use this approximation to eliminate line 16.

The six SEI approximations proposed in this section have allowed us to eliminate lines 1–8 and 50–58 from the CEI. Also, the averages in lines 16, 27 and 28 are eliminated. Terms in lines 41 and 49 are modified based on SEI Approximation 11.3. Remaining terms in Eq. (11.5) that are not a macroscale force-flux pair are those that appear in lines 42–49. An approach for dealing with these terms is developed in the next subsection.

11.4.3 Complex SEI Approximations

The approach to rearranging lines 42–49 is carried out in three stages. First we will consider lines 42–43, which deal with the balance of forces at the fluid-fluid interface. The derivation follows that in [1]. Second, lines 44–47, which provide a balance of forces at the fluid-solid interface, will be rearranged. Finally, the balance of forces at the common curve as described in lines 48–49 will be approximated into a force-flux form. Several SEI approximations will be stated, and the results of Chap. 8 that describe evolution of the geometric variables will be incorporated into the analysis.

wn Interface: Lines 42–43

Lines 42–43 are in the form of an averaging operation over the *wn* interface. This average is denoted $T^{\overline{\overline{wn}}}$ such that

$$\begin{aligned} T^{\overline{\overline{wn}}} =& \Big\langle \big[p_w \mathbf{n}_w + p_n \mathbf{n}_n + \gamma_{wn} \left(\nabla' \cdot \mathbf{l}'_{wn} \right) \\ & + \rho_{wn} \mathbf{g}_{wn} \cdot \left(\mathbf{l} - \mathbf{l}'_{wn} \right) \big] \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \Big\rangle_{\Omega_{wn},\Omega} . \end{aligned} \tag{11.21}$$

The tensor $\mathbf{l}'_{wn}$ was first discussed in the statement of Theorem 2.3 and is defined such that

$$\mathbf{l}'_{wn} = \mathbf{l} - \mathbf{n}_w \mathbf{n}_w \quad \text{for } \mathbf{x} \in \Omega_{wn} . \tag{11.22}$$

Therefore, simple rearrangement gives

$$\mathbf{l} - \mathbf{l}'_{wn} = \mathbf{n}_w \mathbf{n}_w \quad \text{for } \mathbf{x} \in \Omega_{wn} ; \tag{11.23}$$

and the surface divergence is provided as

$$\nabla' \cdot \mathbf{l}'_{wn} = - \left(\nabla' \cdot \mathbf{n}_w \right) \mathbf{n}_w \quad \text{for } \mathbf{x} \in \Omega_{wn} . \tag{11.24}$$

Substitution of these relations into Eq. (11.21) yields

$$T^{\overline{\overline{wn}}} = \Big\langle \left(p_w - p_n - \gamma_{wn} \nabla' \cdot \mathbf{n}_w + \rho_{wn} \mathbf{g}_{wn} \cdot \mathbf{n}_w \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) \Big\rangle_{\Omega_{wn},\Omega} . \tag{11.25}$$

The derivation culminating in Eq. (4.91) shows that the group of terms in the first parentheses in Eq. (11.25) is zero at equilibrium. Additionally, the velocity difference dotted with the unit normal vector is zero at equilibrium. Thus, the quantity within the averaging operator is a microscopic force-flux pair. For use here, it must be transformed to a macroscopic force-flux pair. This transformation involves breaking of the average of the product of microscale quantities so that it is written as a product of macroscale quantities.

To facilitate obtaining an approximate form for $T^{\overline{\overline{wn}}}$, let us first define

$$P_{wn} = p_w - p_n + \rho_{wn} \mathbf{g}_{wn} \cdot \mathbf{n}_w \tag{11.26}$$

and

$$J_w = \nabla' \cdot \mathbf{n}_w \, , \tag{11.27}$$

so that Eq. (11.25) can be written in an abbreviated form as

$$T^{\overline{\overline{wn}}} = \left\langle \left(P_{wn} - \gamma_{wn} J_w \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} . \tag{11.28}$$

We denote macroscale averages of P_{wn} and J_w as P^{wn} and J_w^{wn}, respectively, where

$$P^{wn} = \langle P_{wn} \rangle_{\Omega_{wn},\Omega_{wn}} = p_w^{wn} - p_n^{wn} + \rho^{wn} \left(\mathbf{g}_{wn} \cdot \mathbf{n}_w \right)^{\overline{wn}} \tag{11.29}$$

and

$$J_w^{wn} = \langle J_w \rangle_{\Omega_{wn},\Omega_{wn}} . \tag{11.30}$$

These two expressions may be added in and subtracted out in Eq. (11.28) to facilitate rearrangement, without approximation, to

$$\begin{aligned} T^{\overline{\overline{wn}}} = {} & \left(P^{wn} - \gamma^{wn} J_w^{wn} \right) \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \\ & - \left\langle \gamma^{wn} \left(J_w - J_w^{wn} \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \\ & + \left\langle \left(P_{wn} - P^{wn} \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} \\ & - \left\langle \left(\gamma_{wn} - \gamma^{wn} \right) J_w \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} . \end{aligned} \tag{11.31}$$

The decomposition of Eq. (11.25) into the expression given in Eq. (11.31) is not unique. This latter equation is formulated to have the property that if each of the last three averages of products are expressed as products of averages, they will be zero. Such an approach is appropriate if the difference terms, $J_w - J_w^{wn}$, $P_{wn} - P^{wn}$, and $(\gamma_{wn} - \gamma^{wn}) J_w$, are not correlated to the interface movement, $\mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}})$. In general, however, there is some correlation, so a more thoughtful and careful decomposition of the averages is required. To facilitate the investigation of these last terms, let us write Eq. (11.31) in a more condensed form as

$$T^{\overline{\overline{wn}}} = \left(P^{wn} - \gamma^{wn} J_w^{wn} \right) \left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} - e_J^{\overline{\overline{wn}}} + e_P^{\overline{\overline{wn}}} - e_\gamma^{\overline{\overline{wn}}} \, , \tag{11.32}$$

where

$$e_J^{\overline{\overline{wn}}} = \left\langle \gamma^{wn} \left(J_w - J_w^{wn} \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} , \tag{11.33}$$

$$e_P^{\overline{\overline{wn}}} = \left\langle \left(P_{wn} - P^{wn} \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} , \tag{11.34}$$

and

$$e_\gamma^{\overline{\overline{wn}}} = \left\langle J_w \left(\gamma_{wn} - \gamma^{wn} \right) \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\bar{s}} \right) \right\rangle_{\Omega_{wn},\Omega} . \tag{11.35}$$

The right side of Eq. (11.32) is thus seen to consist of a leading term plus three additional terms that involve deviations between microscale and macroscale variables. The deviations, in order, can be physically interpreted as relating to the relaxation to equilibrium of the curvature, the pressure difference between the phases at the interface, and the interfacial tension. An important attribute of these terms is the time scale over which each of the deviations relaxes. The longest time scale is expected to be for $e_J^{\overline{\overline{wn}}}$, the relaxation of the shape of the interface in response to the forces exerted on it. The pressure difference and the interfacial tension are expected to relax more rapidly, especially when compositional changes are unimportant. The task at hand is to provide approximations for the terms on the right side of Eq. (11.32) that lead to a reasonable macroscale force-flux form for $T^{\overline{\overline{wn}}}$.

To obtain the needed form that is based in physical behavior, we make use of approximations detailed as follows:

SEI Approximation 11.7 (*wn* Interface Conditions)
The four terms that comprise the right side of Eq. (11.32) can be re-expressed making use of the following conditions:

- *The average of the velocity difference satisfies Eq. (8.27) for $\alpha = w$ so that*

$$\left\langle \mathbf{n}_w \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wn},\Omega} = \frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} - \chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t}\,, \tag{11.36}$$

  where use has been made of the fact that $\varepsilon^{\overline{\overline{s}}} = 1 - \varepsilon$, where $\varepsilon = \varepsilon^{\overline{\overline{w}}} + \varepsilon^{\overline{\overline{n}}}$ is the porosity.
- *The slowest relaxation rate term for the fluid-fluid interface is $e_J^{\overline{\overline{wn}}}$, which accounts for changes in the curvature of the interface. This relaxation rate can be approximated as first-order in the deviation from an equilibrium state such that*

$$e_J^{\overline{\overline{wn}}} = -\hat{k}^{wn}\gamma^{wn}\left(\varepsilon^{\overline{\overline{wn}}} - \varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}\right)\,, \tag{11.37}$$

  where $\hat{k}^m$ is a positive coefficient, and $\varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}$ is the wn interfacial area at equilibrium.
- *The relaxation of the pressure and the interfacial tension to their equilibrium values, are accounted for by $e_P^{\overline{\overline{wn}}}$ and $e_\gamma^{\overline{\overline{wn}}}$, respectively. Because both relax on a much smaller time scale than the relaxation of the curvature, these rates can be approximated as*

$$e_P^{\overline{\overline{wn}}} = 0 \tag{11.38}$$

  and

$$e_\gamma^{\overline{\overline{wn}}} = 0\,. \tag{11.39}$$

Making use of Eqs. (11.36)–(11.39) in Eq. (11.32) provides an equation in terms of macroscale quantities,

$$T^{\overline{\overline{wn}}} = \left(P^{wn} - \gamma^{wn}J_w^{wn}\right)\left[\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} - \chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t}\right] + \hat{k}^{wn}\gamma^{wn}\left(\varepsilon^{\overline{\overline{wn}}} - \varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}\right)\,. \tag{11.40}$$

The coefficient $\hat{k}^{wn}$ is a function of system variables. We would like Eq. (11.40) to be in force-flux form. We know that $P^{wn} - \gamma^{wn} J_w^{wn}$ is zero at equilibrium, as previously noted in Eq. (7.131). Therefore, if we define an alternative coefficient, $\hat{k}_1^{wn}$, that is a function of system variables according to

$$\hat{k}^{wn} = \left(\frac{J_w^{wn} \gamma^{wn}}{P^{wn}} - 1 \right) \hat{k}_1^{wn} , \tag{11.41}$$

Equation (11.40) becomes

$$T^{\overline{\overline{wn}}} = (P^{wn} - \gamma^{wn} J_w^{wn}) \left[\frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{w}}}{\mathrm{D}t} - \chi_s^{\overline{\overline{ws}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} - \frac{\gamma^{wn}}{P^{wn}} \hat{k}_1^{wn} \left(\varepsilon^{\overline{\overline{wn}}} - \varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}} \right) \right] . \tag{11.42}$$

This approximation, with P^{wn} replaced by its definition in Eq. (11.29), will be used in lines 42–43 of Eq. (11.5) in obtaining the SEI.

ws and *ns* Interfaces: Lines 44–45 and 46–47

Lines 44–45 deal with the *ws* interface force balance, and lines 46–47 are concerned with the *ns* interface force balance. Because both of these interfaces are fluid-solid interfaces, the analyses of the two different interfaces follow the same pattern. The average quantity of interest is denoted $T^{\overline{\overline{\alpha s}}}$ with

$$T^{\overline{\overline{\alpha s}}} = \left\langle \left[p_\alpha \mathbf{n}_\alpha - \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \mathbf{n}_s + \gamma_{\alpha s} \left(\nabla' \cdot \mathsf{I}'_{\alpha s} \right) + \rho_{\alpha s} \mathbf{g}_{\alpha s} \cdot \left(\mathsf{I} - \mathsf{I}'_{\alpha s} \right) \right] \cdot \left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{\alpha s}, \Omega} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} . \tag{11.43}$$

The unit tensor associated with the interfaces may be expressed in terms of the normal to the solid surface with

$$\mathsf{I} - \mathsf{I}'_{\alpha s} = \mathbf{n}_s \mathbf{n}_s \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} \tag{11.44}$$

and

$$\nabla' \cdot \mathsf{I}'_{\alpha s} = - (\nabla' \cdot \mathbf{n}_s) \mathbf{n}_s \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} . \tag{11.45}$$

Substitution of these two expressions into Eq. (11.43) to eliminate $\mathsf{I}'_{\alpha s}$ yields

$$T^{\overline{\overline{\alpha s}}} = \left\langle \left[- p_\alpha - \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s - \gamma_{\alpha s} \nabla' \cdot \mathbf{n}_s + \rho_{\alpha s} \mathbf{g}_{\alpha s} \cdot \mathbf{n}_s \right] \mathbf{n}_s \cdot \left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{\alpha s}, \Omega} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} . \tag{11.46}$$

Rearrangement of this equation into a mix of microscale and macroscale components now follows identically to Eqs. (11.26) and (11.35) so that we obtain

$$T^{\overline{\overline{\alpha s}}} = - \left(P^{\alpha s} + \gamma^{\alpha s} J_s^{\alpha s} \right) \left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{\alpha s}, \Omega} - e_J^{\overline{\overline{\alpha s}}} - e_P^{\overline{\overline{\alpha s}}} - e_\gamma^{\overline{\overline{\alpha s}}} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} , \tag{11.47}$$

where

$$P_{\alpha s} = p_\alpha + \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s - \rho_{\alpha s}\mathbf{g}_{\alpha s}\cdot\mathbf{n}_s \ , \tag{11.48}$$

$$P^{\alpha s} = \langle P_{\alpha s}\rangle_{\Omega_{\alpha s},\Omega_{\alpha s}} = p_\alpha^{\alpha s} + (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)_s^{\alpha s} + \rho^{\alpha s}(\mathbf{g}_{\alpha s}\cdot\mathbf{n}_s)_s^{\overline{\alpha s}} \ , \tag{11.49}$$

$$J_s = \nabla'\cdot\mathbf{n}_s \ , \tag{11.50}$$

$$J_s^{\alpha s} = \langle J_s\rangle_{\Omega_{\alpha s},\Omega_{\alpha s}} \ , \tag{11.51}$$

$$e_J^{\overline{\overline{\alpha s}}} = \left\langle \gamma^{\alpha s}(J_s - J_s^{\alpha s})\,\mathbf{n}_s\cdot\left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{\alpha s},\Omega} \ , \tag{11.52}$$

$$e_P^{\overline{\overline{\alpha s}}} = \left\langle (P_{\alpha s} - P^{\alpha s})\,\mathbf{n}_s\cdot\left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{\alpha s},\Omega} \ , \tag{11.53}$$

and

$$e_\gamma^{\overline{\overline{\alpha s}}} = \left\langle J_s(\gamma_{\alpha s} - \gamma^{\alpha s})\,\mathbf{n}_s\cdot\left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{\alpha s},\Omega} \ . \tag{11.54}$$

Although the preceding equations are very similar to those for a fluid-fluid interface, the fact that the fluid-solid interfaces are less deformable suggests that we should use different approximations in obtaining the force-flux form. The solid phase in the system is typically only slightly and slowly deformable. Because the solid-surface curvature is determined by the morphology of the solid surface, this curvature also changes slowly with time.[3] In many situations, the curvature of the solid surface will be independent of the fluid phase that contacts it, and this is assumed to be the case here, as in Chap. 8. Finally, we will consider the dynamics of the interface to be slow enough that the average of products in Eqs. (11.52)–(11.54) can be broken into a product of averages. In these cases, the averages of the deviation terms are zero.

Based on the preceding considerations, we state the following SEI approximation:

SEI Approximation 11.8 (*ws* and *ns* Interface Conditions)
The four terms that comprise the right side of Eq. (11.47) can be re-expressed using the following conditions:

- *Neither the deformation of the solid surface nor the curvature of the solid surface is correlated to the fraction of the surface in contact with each fluid phase.*
- *The average of the velocity difference satisfies Eq. (8.22), which can be expressed*

$$\left\langle \mathbf{n}_s\cdot\left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\bar{s}}\right)\right\rangle_{\Omega_{\alpha s},\Omega} = -\chi_s^{\overline{\overline{\alpha s}}}\frac{\mathrm{D}^{\bar{s}}\varepsilon}{\mathrm{D}t} \quad \textit{for } \alpha\in\mathfrak{I}_{\mathrm{f}} \ , \tag{11.55}$$

where $\chi_s^{\overline{\overline{\alpha s}}}$ *is the fraction of the solid surface in contact with fluid phase* α*.*
- *The deviation terms involving curvature, pressure, and interfacial tension are of higher order smallness in comparison to equilibration of forces on the fluid-solid interfaces so that these terms can be approximated as*

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[3] If the solid is being fractured, this approximation will not apply and modeling of the quantity of solid surface and its curvature is much more complicated.

$$e_J^{\overline{\overline{\alpha s}}} = 0 \quad \mathit{for}\ \alpha \in \mathfrak{J}_{\mathrm{f}}\ , \tag{11.56}$$

$$e_P^{\overline{\overline{\alpha s}}} = 0 \quad \mathit{for}\ \alpha \in \mathfrak{J}_{\mathrm{f}}\ , \tag{11.57}$$

and

$$e_\gamma^{\overline{\overline{\alpha s}}} = 0 \quad \mathit{for}\ \alpha \in \mathfrak{J}_{\mathrm{f}}\ . \tag{11.58}$$

Making use of these SEI approximations in Eq. (11.47), we obtain

$$T^{\overline{\overline{\alpha s}}} = \left(P^{\alpha s} + \gamma^{\alpha s} J_s^{\alpha s}\right) \chi_s^{\overline{\overline{\alpha s}}} \frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t} \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{f}}\ . \tag{11.59}$$

This equation, with $P^{\alpha s}$ replaced by its definition from Eq. (11.49), is used with $\alpha = w$ in lines 44–45 of Eq. (11.5) and with $\alpha = n$ in lines 46–47 in obtaining an SEI from the CEI.

wns Common Curve: Lines 48–49

In light of SEI Approximation 11.3, we can identify the term being averaged in lines 48–49 of Eq. (11.5) that requires attention as $T^{\overline{\overline{wns}}}$, where

$$\begin{aligned} T^{\overline{\overline{wns}}} = \Bigg\langle & \Big[\gamma_{wn}\mathbf{n}_{wn} + \gamma_{ws}\mathbf{n}_{ws} + \gamma_{ns}\mathbf{n}_{ns} + \gamma_{wns}\left(\nabla''\cdot\mathsf{I}''_{wns}\right) \\ & - \rho_{wns}\mathbf{g}_{ns}\cdot\left(\mathsf{I} - \mathsf{I}''_{wns}\right) + \mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s\mathbf{n}_s\Big]\cdot\left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right)\Bigg\rangle_{\Omega_{wns},\Omega}\ . \end{aligned} \tag{11.60}$$

The re-expression of $T^{\overline{\overline{wns}}}$ as a macroscale force-flux product requires a bit of finesse because of the different normal vectors that appear. Primary Restriction 11.4 stipulates that the solid surface is smooth such that the normal to the surface, $\mathbf{n}_s$, is unique at every point on Γ_s. For this situation, the needed relations among the normals have been derived in Chap. 4 in Eqs. (4.82)–(4.89). The important results are listed here for convenience.

The unit vector $\mathbf{n}_{wn}$ can be replaced because of its relation to the normal and tangent to the surface with

$$\mathbf{n}_{wn} = \cos\varphi_{ws,wn}\mathbf{n}_{ws} - \sin\varphi_{ws,wn}\mathbf{n}_s \quad \text{for } \mathbf{x} \in \Omega_{wns}\ , \tag{11.61}$$

where $\varphi_{ws,wn}$ is the contact angle between the *ws* and *wn* interfaces. The unit vector $\mathbf{n}_{ns}$ can be replaced because

$$\mathbf{n}_{ns} = -\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns}\ . \tag{11.62}$$

Along the common curve,

$$\nabla''\cdot\mathsf{I}''_{wns} = \kappa_{Nwns}\mathbf{n}_s + \kappa_{Gwns}\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns}\ , \tag{11.63}$$

where κ_{Nwns} and κ_{Gwns} are the normal and geodesic curvatures, respectively. The term $\mathsf{I} - \mathsf{l}''_{wns}$ is expressed in terms of the vectors normal to the common curve as

$$\mathsf{I} - \mathsf{l}''_{wns} = \mathbf{n}_s\mathbf{n}_s + \mathbf{n}_{ws}\mathbf{n}_{ws} \quad \text{for } \mathbf{x} \in \Omega_{wns} \,. \tag{11.64}$$

Substitution of Eqs. (11.61)–(11.64) into Eq. (11.60) followed by minor rearrangement yields

$$\begin{aligned} T^{\overline{\overline{wns}}} = & \Big\langle \big(\gamma_{wn}\cos\varphi_{ws,wn} + \gamma_{ws} - \gamma_{ns} + \gamma_{wns}\kappa_{Gwns} \\ & \qquad - \rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_{ws}\big)\mathbf{n}_{ws}\cdot\big(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\big)\Big\rangle_{\Omega_{wns},\Omega} \\ & - \Big\langle \big(\gamma_{wn}\sin\varphi_{ws,wn} - \gamma_{wns}\kappa_{Nwns} - \mathbf{n}_s\cdot\mathbf{t}_s^{*}\cdot\mathbf{n}_s \\ & \qquad + \rho_{wns}\mathbf{g}_{wns}\cdot\mathbf{n}_s\big)\mathbf{n}_s\cdot\big(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\big)\Big\rangle_{\Omega_{wns},\Omega} \,. \end{aligned} \tag{11.65}$$

To convert this expression to macroscale force-flux form, we propose the following SEI approximation:

SEI Approximation 11.9 (*wns* Common Curve Conditions)
The two averages that comprise the right side of Eq. (11.65) can be re-expressed making use of the following conditions:

- *The product of the factors in the averages over the common curve can be rewritten with negligible error as the average of the product of the two factors.*
- *The average of the velocity difference dotted with* $\mathbf{n}_{ws}$ *in the first average can be approximated by Eq. (8.60) expressed as*

$$\big\langle\mathbf{n}_{ws}\cdot\big(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\big)\big\rangle_{\Omega_{wns},\Omega} = \Big(\epsilon^{\overline{\overline{ws}}} + \epsilon^{\overline{\overline{ns}}}\Big)\frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t} \,, \tag{11.66}$$

where $\chi_s^{\overline{\overline{ws}}}$ *is the fraction of the solid surface in contact with the w phase.*

- *The average of the velocity difference dotted with* $\mathbf{n}_s$ *in the second average can be approximated by Eq. (8.67) expressed as*

$$\big\langle\mathbf{n}_s\cdot\big(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\big)\big\rangle_{\Omega_{wns},\Omega} = -\frac{\epsilon^{\overline{\overline{wns}}}}{\epsilon^{\overline{\overline{ws}}} + \epsilon^{\overline{\overline{ns}}}}\frac{\mathrm{D}^{\overline{s}}\epsilon}{\mathrm{D}t} \,. \tag{11.67}$$

- *The correlations of* γ_{wn} *with* $\cos\varphi_{ws,wn}$ *and* $\sin\varphi_{ws,wn}$ *are negligible so that the average of the products of these factors is equal to the product of the averages.*
- *The correlations of* γ_{wns} *with* κ_{Gwns} *and* κ_{Nwns} *are negligible; so the average of the products of these factors is equal to the product of the averages.*

This approximation relates to the dynamics of the common curve, which is itself an entity of lesser importance in most two-fluid-phase porous medium systems. Therefore, errors associated with the approximations made in modeling this entity should have less impact in developing a good model than errors associated with approximations of the interface and, especially, the phase dynamics.

Based on SEI Approximation 11.9, evaluation of the right side of Eq. (11.65) gives

$$\begin{aligned} T^{\overline{\overline{wns}}} = & \left[\gamma_{wn}^{wns} \cos \varphi^{\overline{\overline{ws,wn}}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} + \gamma^{wns} \kappa_G^{\overline{\overline{wns}}} \right. \\ & \left. - \rho^{wns} \left(\mathbf{g}_{wns} \cdot \mathbf{n}_{ws} \right)^{\overline{wns}} \right] \left(\epsilon^{\overline{\overline{ws}}} + \epsilon^{\overline{\overline{ns}}} \right) \frac{\mathrm{D}^{\overline{s}} \chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t} \\ & + \left[\gamma_{wn}^{wns} \sin \varphi^{\overline{\overline{ws,wn}}} - \gamma^{wns} \kappa_N^{\overline{\overline{wns}}} - \langle \mathbf{n}_s \cdot \mathbf{t}_s^* \cdot \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega_{wns}} \right. \\ & \left. + \rho^{wns} \left(\mathbf{g}_{wns} \cdot \mathbf{n}_s \right)^{\overline{wns}} \right] \frac{\epsilon^{\overline{\overline{wns}}}}{\epsilon^{\overline{\overline{ws}}} + \epsilon^{\overline{\overline{ns}}}} \frac{\mathrm{D}^{\overline{s}} \epsilon}{\mathrm{D}t} \,. \end{aligned} \tag{11.68}$$

The group of terms in the first pair of brackets in this equation accounts for a force imbalance that causes a fluid phase to spread over the solid surface. The group of terms in the second brackets accounts for the forces that act at the common curve normal to the solid surface. Both of these groupings of terms were shown to be zero at equilibrium in the derivations that led to Eqs. (7.134) and (7.135), respectively. Equation (11.68) is used in lines 48–49 of Eq. (11.5) to convert these lines to a macroscale force-flux form in the resulting SEI.

11.4.4 Product Breaking SEI Approximations

The preceding two subsections have provided the SEI approximations needed to obtain an SEI that consists solely of macroscopic force-flux products. However, the averaging operator remains in some of the terms in the resultant SEI. In some instances, it is useful to eliminate this operator, typically acting on a product of microscale quantities, in favor of explicit macroscale products. To accomplish this, some additional SEI approximations will be employed. The line numbers referred to are those in the CEI of Eq. (11.5).

Lines 10, 11, 34, 35, 39, and 40

As a prelude to simplifying these lines, we propose the following:

SEI Approximation 11.10 (Geometric Orientation Products)
Averages of products involving the microscale geometric orientation tensors,

$$\mathsf{G}_\alpha = \mathsf{I} - \mathsf{l}'_\alpha \quad \textit{for } \alpha \in \mathfrak{I}_{\mathrm{I}}, \mathbf{x} \in \Omega_\alpha \tag{11.69}$$

and

$$\mathsf{G}_{wns} = \mathsf{I} - \mathsf{I}''_{wns} \quad \textit{for } \mathbf{x} \in \Omega_{wns} \; , \tag{11.70}$$

and a microscale property, f_α, of the α entity can be approximated as the product of averages of the orientation tensor and f_α such that

$$\langle \mathsf{G}_\alpha f_\alpha \rangle_{\Omega_\alpha,\Omega} = \varepsilon^{\overline{\overline{\alpha}}} \mathsf{G}^\alpha f^\alpha \quad \textit{for } \alpha \in \mathfrak{J}_{\mathrm{I}} \tag{11.71}$$

and

$$\langle \mathsf{G}_{wns} f_{wns} \rangle_{\Omega_{wns},\Omega} = \varepsilon^{\overline{\overline{wns}}} \mathsf{G}^{wns} f^{wns} \; . \tag{11.72}$$

The need for this approximation arises for f corresponding to ρ, γ, and η. For this latter case, we also make use of the definition $\varepsilon^{\overline{\overline{\alpha}}} \eta^\alpha = \eta^{\overline{\overline{\alpha}}}$.

Lines 20, 23, and 26

Products of microscale pressure or surface tension with a velocity difference in the normal direction of an entity may be broken and evaluated as a product of macroscale variables. After breaking the product, use is made of Eq. (11.36) in SEI Approximation 11.7, Eq. (11.55) in SEI Approximation 11.8, and Eqs. (11.66) and (11.67) in SEI Approximation 11.9. We state the approximation as follows:

SEI Approximation 11.11 (Pressure/Tension Products)
The product of a microscale pressure or surface tension of entity α with $\mathbf{n}_\alpha \cdot \left(\mathbf{v}_\kappa - \mathbf{v}^{\overline{s}} \right)$ where $\kappa \in \mathfrak{J}^-_{\mathrm{c}\alpha}$ that is averaged over entity κ may be written as a product of the averages of these factors. The previously developed approximations for the average of the velocity factor may also be invoked. Therefore,

$$\left\langle \mathbf{n}_\alpha \cdot \left(\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}} \right) p_\alpha \right\rangle_{\Omega_{wn},\Omega} = \left(\frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t} - \chi_s^{\overline{\overline{\alpha s}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} \right) p_\alpha^{wn} \quad \textit{for } \alpha \in \mathfrak{J}_{\mathrm{f}} \; , \tag{11.73}$$

$$\left\langle \mathbf{n}_\alpha \cdot \left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\overline{s}} \right) p_\alpha \right\rangle_{\Omega_{\alpha s},\Omega} = \chi_s^{\overline{\overline{\alpha s}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} p_\alpha^{\alpha s} \quad \textit{for } \alpha \in \mathfrak{J}_{\mathrm{f}} \; , \tag{11.74}$$

$$\left\langle \mathbf{n}_s \cdot \left(\mathbf{v}_{\alpha s} - \mathbf{v}^{\overline{s}} \right) \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \right\rangle_{\Omega_{\alpha s},\Omega} = -\chi_s^{\overline{\overline{\alpha s}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} \left(\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \right)_s^{\alpha s} \quad \textit{for } \alpha \in \mathfrak{J}_{\mathrm{f}} \; , \tag{11.75}$$

$$\begin{aligned} \left\langle \mathbf{n}_{wn} \cdot \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}} \right) \gamma_{wn} \right\rangle_{\Omega_{wns},\Omega} = \Bigg[& \left(\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}} \right) \frac{\mathrm{D}^{\overline{s}} \chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t} \cos \varphi^{\overline{\overline{ws,wn}}} \\ & + \frac{\varepsilon^{\overline{\overline{wns}}}}{\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} \sin \varphi^{\overline{\overline{ws,wn}}} \Bigg] \gamma_{wn}^{wns} \; , \end{aligned} \tag{11.76}$$

and

Table 11.1 Lines in CEI Eq. (11.5) that are modified or eliminated by SEIapproximations in deriving the general SEI given by Eq. (11.78). Line numbers not listed are not revised in forming the SEI

Line(s)	SEI Approximation	Impact
1–8	11.1	eliminated
10	11.10	revised
11	11.10	revised
13	11.2	partially eliminated
16	11.6	eliminated
20	11.11	revised
23	11.11	revised
26	11.11	revised
27	11.3, 11.4	partially eliminated
28	11.3, 11.4	eliminated
34–35	11.10	revised
39–40	11.10	revised
41	11.3	revised
42–43	11.7	revised
44–47	11.8	revised
48–49	11.3, 11.9	revised
50	11.3, 11.4	eliminated
51	11.5	eliminated
52–58	11.2	eliminated

$$\left\langle \mathbf{n}_{\alpha s}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\bar{s}}\right)\gamma_{\alpha s}\right\rangle_{\Omega_{wns},\Omega} = \left(\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\bar{s}}\chi_s^{\overline{\overline{\alpha s}}}}{\mathrm{D}t}\gamma_{\alpha s}^{wns} \quad \mathit{for}\ \alpha\in\mathcal{J}_{\mathrm{f}}\,. \tag{11.77}$$

These approximations allow for evaluation of averages that appear in lines 20, 23, and 26 of the CEI in Eq. (11.5).

11.4.5 General SEI

The general SEI is an approximation to the CEI wherein all terms are composed of products of macroscale forces and fluxes. The CEI given as Eq. (11.5) is converted to the SEI by application of the SEI approximations delineated. To assist in following the application of these approximations, Table 11.1 provides the lines of the CEI that are impacted by the SEI approximations. The overall order of lines in the CEI is retained in developing the SEI, but lines are eliminated or revised as indicated in the table. As a consequence, the SEI is written as follows:

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{\alpha}}}+\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}}\tag{1}$$

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\gamma^{\alpha}\left(\mathbf{I}-\mathbf{G}^{\alpha}\right)\right]:\mathbf{d}^{\overline{\overline{\alpha}}}\tag{2}$$

$$+\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left[\varepsilon^{\overline{wns}}\mathbf{t}^{\overline{wns}}+\varepsilon^{\overline{wns}}\gamma^{wns}\left(\mathbf{I}-\mathbf{G}^{wns}\right)\right]:\mathbf{d}^{\overline{wns}}\tag{3}$$

$$-\sum_{\alpha\in\mathfrak{J}}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{g}^{\overline{\overline{\alpha}}}\right)\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\right)\tag{4}$$

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}}\sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}}\overset{\alpha\to\kappa}{M}\left[\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left(\mu^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)-\frac{1}{\theta^{\overline{\overline{\overline{\kappa}}}}}\left(\mu^{\overline{\kappa}}+K_{E}^{\overline{\overline{\kappa}}}+\psi^{\overline{\kappa}}\right)\right]\tag{5}$$

$$+\sum_{\kappa\in\mathfrak{J}_{\mathrm{cs}}}\overset{s\to\kappa}{M}\left[\frac{1}{\theta^{\overline{\overline{\overline{s}}}}}\left(\mu^{\overline{s}}+K_{E}^{\overline{\overline{s}}}+\psi^{\overline{s}}+\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\overline{\mathbf{C}}^{s}}{3j^{s}}\right)-\frac{1}{\theta^{\overline{\overline{\overline{\kappa}}}}}\left(\mu^{\overline{\kappa}}+K_{E}^{\overline{\overline{\kappa}}}+\psi^{\overline{\kappa}}\right)\right]\tag{6}$$

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\overset{\alpha\to wns}{M}\left[\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left(\mu^{\overline{\alpha}}+K_{E}^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)-\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left(\mu^{\overline{wns}}+K_{E}^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\right]\tag{7}$$

$$-\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}}\left\{\overset{\alpha\to wn}{Q}+\overset{\alpha\to wn}{G}+\left(\overline{E}_{\alpha}^{\overline{wn}}+K_{E\alpha}^{\overline{\overline{wn}}}+\psi_{\alpha}^{\overline{wn}}\right)\overset{\alpha\to wn}{M}\right.\tag{8}$$

$$+\left[\overset{\alpha\to wn}{\mathbf{T}}+\frac{\left(\mathbf{v}_{\alpha}^{\overline{wn}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{\alpha\to wn}{M}\right]\cdot\left(\mathbf{v}_{\alpha}^{\overline{wn}}-\mathbf{v}^{\overline{s}}\right)\tag{9}$$

$$\left.+\left(\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{\alpha}}}}{\mathrm{D}t}-\chi_{s}^{\overline{\overline{\alpha s}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t}\right)p_{\alpha}^{wn}\right\}\left(\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}-\frac{1}{\theta^{\overline{\overline{\overline{wn}}}}}\right)\tag{10}$$

$$-\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}}\left\{\overset{\alpha\to\alpha s}{Q}+\overset{\alpha\to\alpha s}{G}+\left(\overline{E}_{\alpha}^{\overline{\alpha s}}+K_{E\alpha}^{\overline{\overline{\alpha s}}}+\psi_{\alpha}^{\overline{\alpha s}}\right)\overset{\alpha\to\alpha s}{M}\right.\tag{11}$$

$$+\left[\overset{\alpha\to\alpha s}{\mathbf{T}}+\frac{\left(\mathbf{v}_{\alpha}^{\overline{\alpha s}}-\mathbf{v}^{\overline{s}}\right)}{2}\overset{\alpha\to\alpha s}{M}\right]\cdot\left(\mathbf{v}_{\alpha}^{\overline{\alpha s}}-\mathbf{v}^{\overline{s}}\right)\tag{12}$$

$$\left.+\chi_{s}^{\overline{\overline{\alpha s}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t}p_{\alpha}^{\alpha s}\right\}\left(\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}-\frac{1}{\theta^{\overline{\overline{\overline{\alpha s}}}}}\right)\tag{13}$$

$$
\begin{aligned}
&-\sum_{\kappa\in\mathfrak{J}_{\mathrm{cs}}} \left\{ \overset{s\rightarrow\kappa}{Q} + \overset{s\rightarrow\kappa}{G} + \left(\overline{E}_s^{\overline{\kappa}} + K_{Es}^{\overline{\overline{\kappa}}} + \psi_s^{\overline{\kappa}}\right) \overset{s\rightarrow\kappa}{M} \right. \\
&\qquad + \left[\overset{s\rightarrow\kappa}{\mathbf{T}} + \frac{\left(\mathbf{v}_s^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right)}{2} \overset{s\rightarrow\kappa}{M} \right] \cdot \left(\mathbf{v}_s^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right) \\
&\qquad \left. - \chi_s^{\overline{\overline{\kappa}}} \frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t} \left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\right)^{\kappa} \right\} \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right) \\
&- \left\{ \overset{wn\rightarrow wns}{Q} + \overset{wn\rightarrow wns}{G} + \left(\overline{E}_{wn}^{\overline{wns}} + K_{Ewn}^{\overline{\overline{wns}}} + \psi_{wn}^{\overline{wns}}\right) \overset{wn\rightarrow wns}{M} \right. \\
&\qquad + \left[\overset{wn\rightarrow wns}{\mathbf{T}} + \frac{\left(\mathbf{v}_{wn}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right)}{2} \overset{wn\rightarrow wns}{M} \right] \cdot \left(\mathbf{v}_{wn}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right) \\
&\qquad + \left[\left(\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}}\right) \frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{ws}}}}{\mathrm{D}t} \cos\varphi^{\overline{\overline{ws,wn}}} \right. \\
&\qquad\qquad \left. \left. + \frac{\varepsilon^{\overline{\overline{wns}}}}{\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}}} \frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t} \sin\varphi^{\overline{\overline{ws,wn}}} \right] \gamma_{wn}^{wns} \right\} \left(\frac{1}{\theta^{\overline{\overline{wn}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}} \right) \\
&-\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}} \left\{ \overset{\alpha s\rightarrow wns}{Q} + \overset{\alpha s\rightarrow wns}{G} + \left(\overline{E}_{\alpha s}^{\overline{wns}} + K_{E\alpha s}^{\overline{\overline{wns}}} + \psi_{\alpha s}^{\overline{wns}}\right) \overset{\alpha s\rightarrow wns}{M} \right. \\
&\qquad + \left[\overset{\alpha s\rightarrow wns}{\mathbf{T}} + \frac{\left(\mathbf{v}_{\alpha s}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right)}{2} \overset{\alpha s\rightarrow wns}{M} \right] \cdot \left(\mathbf{v}_{\alpha}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right) \\
&\qquad \left. + \left(\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}}\right) \frac{\mathrm{D}^{\overline{s}}\chi_s^{\overline{\overline{\alpha s}}}}{\mathrm{D}t} \gamma_{\alpha s}^{wns} \right\} \left(\frac{1}{\theta^{\overline{\overline{\alpha s}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}} \right) \\
&- \overset{s\rightarrow wns}{Q^*} \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}} \right) \\
&-\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \eta^{\overline{\overline{\alpha}}} \nabla\theta^{\overline{\overline{\alpha}}} - \nabla\left(\varepsilon^{\overline{\overline{\alpha}}} p^{\alpha}\right) + \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \nabla\left(\mu^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right) + \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \mathbf{g}^{\overline{\alpha}} \right. \\
&\qquad \left. - \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}^{-}} \left[\overset{\alpha\rightarrow\kappa}{\mathbf{T}} - \frac{\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)}{2} \overset{\alpha\rightarrow\kappa}{M} + \left(\mathbf{v}_{\alpha}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right) \overset{\alpha\rightarrow\kappa}{M} \right] \right\} \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) \\
&-\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \eta^{\overline{\overline{\alpha}}} \left(\mathsf{I} - \mathsf{G}^{\alpha}\right) \cdot \nabla\theta^{\overline{\overline{\alpha}}} + \nabla\cdot \left[\left(\mathsf{I} - \mathsf{G}^{\alpha}\right) \varepsilon^{\overline{\overline{\alpha}}} \gamma^{\alpha} \right] \right. \\
&\qquad + \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \left(\mathsf{I} - \mathsf{G}^{\alpha}\right) \cdot \nabla\left(\mu^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right) + \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \mathbf{g}^{\overline{\alpha}} \\
&\qquad + \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}^{+}} \left[\overset{\kappa\rightarrow\alpha}{\mathbf{T}} - \frac{\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)}{2} \overset{\kappa\rightarrow\alpha}{M} + \left(\mathbf{v}_{\kappa}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) \overset{\kappa\rightarrow\alpha}{M} \right]
\end{aligned}
$$

$$
\begin{aligned}
&\left. - \left[\overset{\alpha\to wns}{\mathbf{T}} - \frac{\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)}{2} \overset{\alpha\to wns}{M} + \left(\mathbf{v}_{\alpha}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right) \overset{\alpha\to wns}{M} \right] \right\} \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) \\
&- \frac{1}{\theta^{\overline{\overline{\overline{wns}}}}} \left\{ \eta^{\overline{\overline{wns}}} \left(\mathsf{I} - \mathsf{G}^{wns}\right) \cdot \nabla \theta^{\overline{\overline{wns}}} - \nabla \cdot \left[\left(\mathsf{I} - \mathsf{G}^{wns}\right) \varepsilon^{\overline{\overline{wns}}} \gamma^{wns} \right] \right. \\
&\quad + \varepsilon^{\overline{\overline{wns}}} \rho^{wns} \left(\mathsf{I} - \mathsf{G}^{wns}\right) \cdot \nabla \left(\mu^{\overline{wns}} + K_E^{\overline{\overline{wns}}} + \psi^{\overline{wns}} \right) + \varepsilon^{\overline{\overline{wns}}} \rho^{wns} \mathbf{g}^{\overline{wns}} \\
&\quad + \sum_{\kappa \in \mathfrak{I}^{+}_{\mathrm{cwns}}} \left[\overset{\kappa\to wns}{\mathbf{T}} - \frac{\left(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right)}{2} \overset{\kappa\to wns}{M} + \left(\mathbf{v}_{\kappa}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right) \overset{\kappa\to wns}{M} \right] \\
&\quad \left. - \langle \mathbf{n}_s \cdot \mathbf{t}_s^{*} \cdot \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega} \right\} \cdot \left(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right) \\
&+ \frac{1}{\theta^{\overline{\overline{\overline{wn}}}}} \left[\frac{\mathrm{D}^{\overline{s}} \varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} - \chi_s^{\overline{\overline{ws}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} - \frac{\gamma^{wn} \hat{k}_1^{wn} \left(\varepsilon^{\overline{\overline{wn}}} - \varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}} \right)}{p_w^{wn} - p_n^{wn} + \rho^{wn} \left(\mathbf{g}_{wn} \cdot \mathbf{n}_w\right)^{\overline{wn}}} \right] \\
&\qquad\qquad \times \left(p_w^{wn} - p_n^{wn} + \rho^{wn} \left(\mathbf{g}_{wn} \cdot \mathbf{n}_w\right)^{\overline{wn}} - \gamma^{wn} J_w^{wn} \right) \\
&+ \frac{1}{\theta^{\overline{\overline{\overline{ws}}}}} \chi_s^{\overline{\overline{ws}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} \left[p_w^{ws} + \left(\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s\right)_s^{ws} - \rho^{ws} \left(\mathbf{g}_{ws} \cdot \mathbf{n}_s\right)^{\overline{ws}} + \gamma^{ws} J_s^{ws} \right] \\
&+ \frac{1}{\theta^{\overline{\overline{\overline{ns}}}}} \chi_s^{\overline{\overline{ns}}} \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} \left[p_n^{ns} + \left(\mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s\right)_s^{ns} - \rho^{ns} \left(\mathbf{g}_{ns} \cdot \mathbf{n}_s\right)^{\overline{ns}} + \gamma^{ns} J_s^{ns} \right] \\
&- \frac{1}{\theta^{\overline{\overline{\overline{wns}}}}} \left(\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}} \right) \frac{\mathrm{D}^{\overline{s}} \chi_{ws}^{ss}}{\mathrm{D}t} \left[\gamma_{wn}^{wns} \cos \varphi^{\overline{\overline{ws,wn}}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} \right. \\
&\qquad\qquad \left. + \gamma^{wns} \kappa_G^{\overline{\overline{wns}}} - \rho^{wns} \left(\mathbf{g}_{wns} \cdot \mathbf{n}_{ws}\right)^{\overline{wns}} \right] \\
&- \frac{1}{\theta^{\overline{\overline{\overline{wns}}}}} \left(\frac{\varepsilon^{\overline{\overline{wns}}}}{\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}}} \right) \frac{\mathrm{D}^{\overline{s}} \varepsilon}{\mathrm{D}t} \left[\gamma_{wn}^{wns} \sin \varphi^{\overline{\overline{ws,wn}}} - \gamma^{wns} \kappa_N^{\overline{\overline{wns}}} \right. \\
&\qquad\qquad \left. - \langle \mathbf{n}_s \cdot \mathbf{t}_s^{*} \cdot \mathbf{n}_s \rangle_{\Omega_{wns}, \Omega_{wns}} + \rho^{wns} \left(\mathbf{g}_{wns} \cdot \mathbf{n}_s\right)^{\overline{wns}} \right] = \sum_{\alpha \in \mathfrak{I}} \Lambda^{\overline{\overline{\alpha}}} \geq 0 \,.
\end{aligned}
\tag{11.78}
$$

Equation (11.78) is a general SEI that descends from the CEI but is dependent on the SEI approximations employed. Equation (11.78) is useful for developing closure relations for two-fluid-phase flow in a porous medium when thermal gradients may exist in the entities and different entities may have different temperatures at a macroscopic point. Although mass exchange between entities has not been precluded, successful modeling of this process can be better achieved if one formulates a multi-species model. This is a more general case than considered here and is accompanied by more complex equations. Nevertheless, based on the multispecies analysis of Chap. 10 and the multiphase approach of the current chapter, the formulation of a multispecies, multi-fluid-phase model can be undertaken following the TCAT formalism.

11.5 Example Application

Equation (11.78) is a rich equation that can be exploited to obtain and investigate closure relations for a wide range of problems. Our objective here is not to illustrate the most complex problem possible. Rather, we will apply some secondary restrictions that simplify the SEI for a class of problems of interest. We will then proceed to close the equation set as an illustration for use in modeling two-fluid-phase flow. If one is interested in a more complex case of a two-fluid-phase system than that considered subsequently, it is possible to return to the general SEI of Eq. (11.78) and consider a less restrictive set of secondary restrictions. If the SEI approximations already employed are deemed inappropriate, one can work from the CEI given as Eq. (11.5) and apply an alternative set of SEI approximations. For a more general problem, for example if species transport is of interest or if a different thermodynamic theory is desired, it will be necessary to construct a CEI using the general TCAT formalism as as been described.

11.5.1 Selection of Secondary Restrictions

The secondary restrictions specify the processes that are of interest in the analysis to be performed. Although they simplify the SEI, they are not approximate relations. They simply eliminate processes that are not going to be modeled.

We will consider the case where the system is isothermal, the entities do not exchange mass, and the mass densities of the interfaces and common curve are zero. These conditions are stated formally in the following secondary restrictions:

Secondary Restriction 11.1 (Isothermal)
The system is isothermal such that $\theta^{\overline{\overline{\alpha}}} = \theta_{\alpha}^{\overline{\overline{\kappa}}} = \theta^{\cdot}$ *for* $\alpha \in \mathfrak{I}$, $\kappa \in \mathfrak{I}_{c\alpha}^{-}$*; and all derivatives of* $\theta^{\cdot}$ *are zero.*

Secondary Restriction 11.2 (No Mass Exchange)
The entities of the system are strictly immiscible and do not exchange mass, so $\overset{\alpha\rightarrow\kappa}{M} = 0$ *for all* $\alpha \in \mathfrak{I}$ *and* $\kappa \in \mathfrak{I}_{c\alpha}^{-}$*.*

Secondary Restriction 11.3 (Massless Interfaces and Common Curve)
The mass densities of the interfaces and common curves are zero such that $\rho^{\alpha} = 0$ *for* $\alpha \in \mathfrak{I}_{\mathrm{I}}$ *and* $\rho^{wns} = 0$*.*

We emphasize that these conditions are not necessary for proceeding to a closed system of equations, they are merely conditions that pertain to the physical system we wish to illustrate.

With these three secondary restrictions applied to the general SEI given as Eq. (11.78), we obtain the simplified SEI,

$$
\begin{aligned}
&+\sum_{\alpha\in\mathcal{J}_{\mathrm{f}}}\frac{1}{\theta}\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}\mathbf{I}\right):\mathbf{d}^{\overline{\overline{\alpha}}}+\frac{1}{\theta}\left(\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right):\mathbf{d}^{\overline{\overline{s}}}\\
&+\sum_{\alpha\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta}\left[\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\gamma^{\alpha}\left(\mathbf{I}-\mathbf{G}^{\alpha}\right)\right]:\mathbf{d}^{\overline{\overline{\alpha}}}\\
&+\frac{1}{\theta}\left[\varepsilon^{\overline{\overline{wns}}}\mathbf{t}^{\overline{\overline{wns}}}+\varepsilon^{\overline{\overline{wns}}}\gamma^{wns}\left(\mathbf{I}-\mathbf{G}^{wns}\right)\right]:\mathbf{d}^{\overline{\overline{wns}}}\\
&+\sum_{\alpha\in\mathcal{J}_{\mathrm{f}}}\frac{1}{\theta}\left\{\nabla\left(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}\right)-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\left(\mu^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\right.\\
&\qquad\qquad\left.+\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}^{-}}\overset{\alpha\to\kappa}{\mathbf{T}}\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&-\sum_{\alpha\in\mathcal{J}_{\mathrm{I}}}\frac{1}{\theta}\left\{\nabla\cdot\left[\left(\mathbf{I}-\mathbf{G}^{\alpha}\right)\varepsilon^{\overline{\overline{\alpha}}}\gamma^{\alpha}\right]+\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}^{+}}\overset{\kappa\to\alpha}{\mathbf{T}}-\overset{\alpha\to wns}{\mathbf{T}}\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&+\frac{1}{\theta}\left\{\nabla\cdot\left[\left(\mathbf{I}-\mathbf{G}^{wns}\right)\varepsilon^{\overline{\overline{wns}}}\gamma^{wns}\right]-\sum_{\kappa\in\mathcal{J}_{\mathrm{cwns}}^{+}}\overset{\kappa\to wns}{\mathbf{T}}\right.\\
&\qquad\qquad\left.+\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^{*}\cdot\mathbf{n}_s\mathbf{n}_s\right\rangle_{\Omega_{wns},\Omega}\right\}\cdot\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\\
&+\frac{1}{\theta}\left[\frac{\mathrm{D}^{\overline{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t}-\chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t}-\frac{\gamma^{wn}\hat{k}_1^{wn}\left(\varepsilon^{\overline{\overline{wn}}}-\varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}\right)}{\left(p_w^{wn}-p_n^{wn}\right)}\right]\left(p_w^{wn}-p_n^{wn}-\gamma^{wn}J_w^{wn}\right)\\
&+\frac{1}{\theta}\frac{\mathrm{D}^{\overline{s}}\varepsilon}{\mathrm{D}t}\left[\chi_s^{\overline{\overline{ws}}}p_w^{ws}+\chi_s^{\overline{\overline{ns}}}p_n^{ns}+\chi_s^{\overline{\overline{ws}}}\left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\right)_s^{ws}+\chi_s^{\overline{\overline{ns}}}\left(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\right)_s^{ns}\right.\\
&\qquad+\chi_s^{\overline{\overline{ws}}}\gamma^{ws}J_s^{ws}+\chi_s^{\overline{\overline{ns}}}\gamma^{ns}J_s^{ns}\\
&\qquad\left.-\left(\frac{\varepsilon^{\overline{\overline{wns}}}}{\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}}\right)\left(\gamma_{wn}^{wns}\sin\varphi^{\overline{\overline{ws,wn}}}-\gamma^{wns}\kappa_N^{\overline{\overline{wns}}}-\left(\mathbf{n}_s\cdot\mathbf{t}_s^{*}\cdot\mathbf{n}_s\right)^{wns}\right)\right]\\
&-\frac{1}{\theta}\left(\varepsilon^{\overline{\overline{ws}}}+\varepsilon^{\overline{\overline{ns}}}\right)\frac{\mathrm{D}^{\overline{s}}\chi_{ws}^{ss}}{\mathrm{D}t}\left[\gamma_{wn}^{wns}\cos\varphi^{\overline{\overline{ws,wn}}}+\gamma_{ws}^{wns}-\gamma_{ns}^{wns}+\gamma^{wns}\kappa_G^{\overline{\overline{wns}}}\right]\\
&=\sum_{\alpha\in\mathcal{J}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,.
\end{aligned}
\tag{11.79}
$$

11.5.2 Identification of Variables

The variables that appear in the equations are similar to those listed for the single-fluid-phase flow case of Eq. (9.64). Here, the set is expanded because of the presence of additional phases, interfaces, and the common curve. For convenience, we list the variables as three sets, $\mathcal{V}_{\mathrm{P}}$, $\mathcal{V}_{\mathrm{I}}$, and $\mathcal{V}_{\mathrm{C}}$, accounting, respectively, for properties of phases, interfaces, and the common curve. These sets are

$$\begin{aligned}\mathcal{V}_{\mathrm{P}} = \Big\{&\varepsilon^{\overline{\overline{\alpha}}}, \rho^{\alpha}, \mathbf{v}^{\overline{\alpha}}, \mathbf{g}^{\overline{\alpha}}, \overset{\alpha\to\kappa}{\mathbf{T}}, \mathbf{t}^{\overline{\overline{\alpha}}}, \mathbf{t}^{s}, p^{\beta}, p_{\beta}^{wn}, p_{\beta}^{\beta s}, (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)_s^{\beta s}, (\mathbf{n}_s\cdot\mathbf{t}_s^{*}\cdot\mathbf{n}_s)_s^{wns},\\ &\langle\mathbf{n}_s\cdot\mathbf{t}_s^{*}\cdot\mathbf{n}_s\mathbf{n}_s\rangle_{\Omega_{wns},\Omega}, K_E^{\overline{\overline{\beta}}}, \mu^{\overline{\beta}}, \psi^{\overline{\beta}}, \Lambda^{\alpha}\Big\} \quad \text{for } \alpha\in\mathcal{I}_{\mathrm{P}}, \kappa\in\mathcal{I}_{\mathrm{c}\alpha}^{-}, \beta\in\mathcal{I}_{\mathrm{f}}\,,\end{aligned} \tag{11.80}$$

$$\begin{aligned}\mathcal{V}_{\mathrm{I}} = \Big\{&\varepsilon^{\overline{\overline{\alpha}}}, \mathbf{v}^{\overline{\alpha}}, \overset{\alpha\to wns}{\mathbf{T}}, \gamma^{\alpha}, \gamma_{\alpha}^{wns}, \mathbf{G}^{\alpha}, J_w^{wn}, J_s^{ws}, J_s^{ns},\\ &\chi_s^{\overline{\overline{ws}}}, \chi_s^{\overline{\overline{ns}}}, \varphi^{\overline{\overline{ws,wns}}}\Big\} \quad \text{for } \alpha\in\mathcal{I}_{\mathrm{I}}\,,\end{aligned} \tag{11.81}$$

and

$$\mathcal{V}_{\mathrm{C}} = \Big\{\varepsilon^{\overline{\overline{wns}}}, \mathbf{v}^{\overline{wns}}, \gamma^{wns}, \mathbf{G}^{wns}, \kappa_N^{\overline{\overline{wns}}}, \kappa_G^{\overline{\overline{wns}}}\Big\}\,. \tag{11.82}$$

Solution for these variables is accomplished by a combination of imposed conditions, conservation equations (from Table 6.3), evolution equations (Eqns (8.58), (8.59), (8.69), and (8.73) subject to the normal velocity approximations of Sect. 8.7), and closure relations (to be determined subsequently). The imposed conditions include sophisticated proposals, such as equations of state, and more direct approximate specifications (e.g., $K_E^{\overline{\overline{\beta}}} = 0$ or $p_{\beta}^{wn} = p^{\beta}$). Enough conditions must be imposed to make up for the deficit in equations that exists between the number of variables and the number of conservation, evolution, and closure equations[4]. The actual count of variables and imposition of conditions is left as an exercise. The process involved is analogous to that detailed in Sect. 9.6.3.

11.5.3 Specification of Closure Conditions

The SEI of Eq. (11.79) consists of a sum of pairs of fluxes multiplied by forces, where the flux is always listed first in each pairing. All the fluxes and forces are zero at equilibrium. Additionally, the forces and fluxes are independent such that it is possible for only one of the products to be non-zero. Because the entropy generation rate must be non-negative for any condition, this means that each force-flux pair must itself be non-negative. Thus, as a first approach to obtaining closure re-

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[4] In determining this deficit, it is important to recognize that no mass conservation equations for the interface and common curve exist; all terms in these equations are zero because of Secondary Restrictions 11.2 and 11.3. Additionally, because the system is isothermal as per Secondary Restriction 11.1, the energy equations are not closed or employed in the resulting model.

lations, we can consider fluxes to be linear functions of the forces. This approach provides closure conditions whose utility can be analyzed in a problem of interest by comparing observed and predicted behaviors. If the comparison is not satisfactory, a more general closure relation can be developed based on insights from subscale simulation, computer modeling of the macroscale equations, experimental data, and physical insights. Indeed, to account for the physics of complex process, integration of all sources of information is essential to obtaining a satisfactory model.

Here, we will develop closure relations by specifying that the fluxes be either zero order or first order in the forces. In general, each flux could be proposed to be linear in the full set of forces. However, we will make use of insights regarding some of the important processes to propose a more restricted formulation with each flux being proposed to be linear in a subset of the forces. We will consider the fluxes in the order in which they appear in Eq. (11.79).

Lines 1–3: Stress Tensor

Lines 1–3 of Eq. (11.79) involve relations between the stress tensors and the rates of strain. Although microscale gradients in velocity contribute to the microscale stress tensor, at the macroscale this impact on the flow is accounted for by interactions among the phases. Thus, macroscale velocity gradients do not contribute significantly to the macroscale stress tensor. This is accounted for by considering that the equilibrium form of the stress tensor also applies away from equilibrium. Thus the fluxes, the quantities that are multiplied with the rate of strain tensors, are approximated as

$$\mathbf{t}^{\overline{\overline{\alpha}}} = -p^{\alpha} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} \,, \tag{11.83}$$

$$\mathbf{t}^{\overline{\overline{s}}} = \mathbf{t}^{s} \,, \tag{11.84}$$

$$\mathbf{t}^{\overline{\overline{\alpha}}} = (\mathbf{I} - \mathbf{G}^{\alpha})\,\gamma^{\alpha} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{I}} \,, \tag{11.85}$$

and

$$\mathbf{t}^{\overline{\overline{wns}}} = -\,(\mathbf{I} - \mathbf{G}^{wns})\,\gamma^{wns} \,. \tag{11.86}$$

The presence of the geometric variable $\mathbf{G}^{\alpha}$ for the interface and common curve stress tensors is consistent with the change in dimensionality of the tensors that occurs in conjunction with the averaging procedure. For the case where the associated microscale interfaces and common curve have no preferred orientation, $\mathbf{G}^{\alpha} = \mathbf{I}/3$ for $\alpha \in \mathfrak{I}_{\mathrm{I}}$, and $\mathbf{G}^{wns} = 2\mathbf{I}/3$.

Lines 4–8: Fluxes with $\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}$ as Conjugate Forces

In lines 4–8 of Eq. (11.79), the velocities relative to the solid-phase velocity are the forces. A significant element of the flux is the term of the form $\overset{\alpha\to\kappa}{\mathbf{T}}$, which accounts for momentum exchange between entities. Because the interfaces are massless, and thus have no momentum, it seems that any momentum transferred from a fluid phase to the interface must immediately be transferred to the adjacent phase. From a physical point of view, this means that one phase is able to drag another phase along with its flow. For this reason, we will consider the fluxes associated with the phases to be proportional to both of the fluid phase relative velocities. An interface can move not only because of internal forces, but also because adjacent phases may apply external forces when they move. Therefore, the interface velocities are considered to be dependent on the adjacent phase velocities. Similarly, we will consider the fluxes associated with the common curve to be proportional to its conjugate force, $\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}$, and the forces of the relative phase velocities. The interphase velocities themselves could be included as contributing to common curve motion for generality, but this effect is ignored here in the interest of simplicity. Also, in the linearization process, the terms $K_E^{\overline{\overline{\alpha}}}$ drop out because they are higher order in velocity. Thus we obtain

$$\begin{aligned}
&\nabla\left(\varepsilon^{\overline{\overline{\alpha}}} p^{\alpha}\right) - \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \nabla\left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}}\right) - \varepsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \mathbf{g}^{\overline{\alpha}} + \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\alpha}^{-}} \overset{\alpha\to\kappa}{\mathbf{T}} \\
&\qquad = \sum_{\kappa \in \mathfrak{I}_{\mathrm{f}}} \hat{\mathsf{R}}_{\kappa}^{\alpha} \cdot \left(\mathbf{v}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right) \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} ,
\end{aligned} \tag{11.87}$$

$$\begin{aligned}
&\nabla\cdot\left[\left(\mathsf{I} - \mathsf{G}^{\alpha}\right) \varepsilon^{\overline{\overline{\alpha}}} \gamma^{\alpha}\right] + \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\alpha}^{+}} \overset{\kappa\to\alpha}{\mathbf{T}} - \overset{\alpha\to wns}{\mathbf{T}} \\
&\qquad = -\hat{\mathsf{R}}_{\alpha}^{\alpha} \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right) - \sum_{\kappa \in \mathfrak{I}_{\mathrm{c}\alpha}^{+}} \hat{\mathsf{R}}_{\kappa}^{\alpha} \cdot \left(\mathbf{v}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right) \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{I}} ,
\end{aligned} \tag{11.88}$$

and

$$\begin{aligned}
&\nabla\cdot\left[\left(\mathsf{I} - \mathsf{G}^{wns}\right) \varepsilon^{\overline{\overline{wns}}} \gamma^{wns}\right] - \sum_{\kappa \in \mathfrak{I}_{\mathrm{cwns}}^{+}} \overset{\kappa\to wns}{\mathbf{T}} - \overset{s\to wns}{\mathbf{T}^{*}} \\
&\qquad = \hat{\mathsf{R}}_{wns}^{wns} \cdot \left(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right) + \sum_{\kappa \in \mathfrak{I}_{\mathrm{f}}} \hat{\mathsf{R}}_{\kappa}^{wns} \cdot \left(\mathbf{v}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}\right) .
\end{aligned} \tag{11.89}$$

In these expressions, the resistance coefficients, $\hat{\mathsf{R}}$, are symmetric second-order tensors with $\hat{\mathsf{R}}_{\alpha}^{\alpha}$ positive, semi-definite. Additionally, use has been made of Eqs. (6.98) and (11.14) to replace $\langle \mathbf{n}_s \cdot \mathbf{t}_s^{*} \cdot \mathbf{n}_s \mathbf{n}_s \rangle_{\Omega_{wns},\Omega}$ with $-\overset{s\to wns}{\mathbf{T}^{*}}$ in Eq. (11.89).

Line 9: Capillary Pressure

Line 9 of Eq. (11.79) involves a force that is a relaxation of the capillary pressure (the product of the interfacial tension and curvature of the *wn* interface) to its equilibrium value, the difference in the pressures of the two fluid phases at that interface. The linearized closure relation is

$$\frac{\mathrm{D}^{\bar{s}}\varepsilon^{\overline{\overline{w}}}}{\mathrm{D}t} - \chi_s^{\overline{\overline{ws}}}\frac{\mathrm{D}^{\bar{s}}\varepsilon}{\mathrm{D}t} - \frac{\gamma^{wn}\hat{k}_1^{wn}\left(\varepsilon^{\overline{\overline{wn}}} - \varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}\right)}{\left(p_w^{wn} - p_n^{wn}\right)} = \hat{c}^{wn}\left(p_w^{wn} - p_n^{wn} - \gamma^{wn}J_w^{wn}\right) . \tag{11.90}$$

This equation indicates that when any volume fraction changes occur at a longer time scale, the relaxation of the capillary pressure so that it balances the fluid pressures is accompanied primarily by a change in the amount of *wn* interfacial area per volume.

Lines 10–12: Force Balance on Solid Surface

Linearization of the force-flux product of lines 10–12 of Eq. (11.79) gives

$$\begin{aligned}\frac{\mathrm{D}^{\bar{s}}\varepsilon}{\mathrm{D}t} = \hat{c}^{ss}\Bigg[&\chi_s^{\overline{\overline{ws}}}p_w^{ws} + \chi_s^{\overline{\overline{ns}}}p_n^{ns} + (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)^{ss} + \left(\chi_s^{\overline{\overline{ws}}}\gamma^{ws} + \chi_s^{\overline{\overline{ns}}}\gamma^{ns}\right)J_s^{ss} \\ &- \left(\frac{\varepsilon^{\overline{\overline{wns}}}}{\varepsilon^{\overline{\overline{ws}}} + \varepsilon^{\overline{\overline{ns}}}}\right)\left(\gamma_{wn}^{wns}\sin\varphi^{\overline{\overline{ws,wn}}} - \gamma^{wns}\kappa_N^{\overline{\overline{wns}}} - (\mathbf{n}_s\cdot\mathbf{t}_s^{*}\cdot\mathbf{n}_s)^{wns}\right)\Bigg] ,\end{aligned} \tag{11.91}$$

where use has been made of SEI Approximation 11.8, which requires that

$$\chi_s^{\overline{\overline{ws}}}(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)_s^{ws} + \chi_s^{\overline{\overline{ns}}}(\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)_s^{ns} = (\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s)_s^{ss} \tag{11.92}$$

and

$$J_s^{ws} = J_s^{ns} = J_s^{ss} . \tag{11.93}$$

Equation (11.91) states that a change in porosity can occur due to a disequilibrium of the normal forces on the solid surface. The first group of terms accounts for a disequilibrium between the fluid and the normal stress on the solid surface with a small correction due to solid surface tension effects. The second group of terms accounts for any disequilibrium in the normal forces at the common curve.

Line 13: Spreading Force

A linear dependence of the flux in line 13 of Eq. (11.79) on its conjugate force provides the linear relation

$$\frac{\mathrm{D}^{\bar{s}}\chi_{ws}^{ss}}{\mathrm{D}t} = -\hat{c}^{wns}\left[\gamma_{wn}^{wns}\cos\varphi^{\overline{\overline{ws,wn}}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} + \gamma^{wns}\kappa_G^{\overline{\overline{wns}}}\right] . \tag{11.94}$$

This equation accounts for an imbalance in the surface tension forces acting tangentially to the solid surface at the common curve. When the forces are not in balance, they cause the common curve to move, thereby changing the fraction of the solid surface that is in contact with each of the fluid phases.

11.5.4 Closed Set of Conservation Equations

With the conditions imposed by the SEI approximations, by secondary restrictions, and in linearizing the force-flux relations in the SEI, the closure relations complete the specification of the conservation equations to be solved. We note that Eqs. (11.90), (11.91), and (11.94) are most easily incorporated into the problem description notationally as additional equations rather than by using them to eliminate rates of change of the associated geometric properties. We will apply the secondary restrictions and the other closure relations to the mass and momentum equations given in Table 6.3.

Mass Conservation Equations

Secondary restriction 11.2 specifies that no mass exchange occurs between entities. Secondary restriction 11.3 requires that the interfaces and common curve be massless. By these two restrictions, all terms in the interface and common curve mass conservation equations are zero such that the equations are trivial. Mass conservation equations survive for the three phases of the system and take the form

$$\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha})}{\mathrm{D}t}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}=0 \quad \text{for } \alpha\in\mathcal{J}_{\mathrm{P}}\,. \tag{11.95}$$

Momentum Conservation for the Fluid Phases

The momentum conservation equations for the *w* and *n* phases make use of the closure relations for the stress tensor given in Eq. (11.83) and the closure relation of Eq. (11.87). Substitution of these two equations into the general momentum equation from Table 6.3 under conditions of no mass exchange yields

$$\begin{aligned}\frac{\mathrm{D}^{\overline{\alpha}}(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}})}{\mathrm{D}t}&+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}\right)\\&+\hat{\mathsf{R}}^{\alpha}_{w}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)+\hat{\mathsf{R}}^{\alpha}_{n}\cdot\left(\mathbf{v}^{\overline{n}}-\mathbf{v}^{\overline{s}}\right)=\mathbf{0}\quad\text{for } \alpha\in\mathcal{J}_{\mathrm{f}}\,.\end{aligned} \tag{11.96}$$

For the case of slow flow, the first two terms in this equation are zero. The remaining terms provide a Darcy-like expression for flow being proportional to a potential gradient with the added feature of coupling between the two fluid phases.

Momentum Conservation for the Interfaces

For massless interfaces, the momentum equation in conjunction with the stress tensor given by Eq. (11.85) and the closure relation of Eq. (11.88) provides the condition

$$\hat{\mathsf{R}}^{\alpha}_{\alpha}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)+\sum_{\kappa\in\mathfrak{J}^{+}_{\mathrm{c}\alpha}}\hat{\mathsf{R}}^{\alpha}_{\kappa}\cdot\left(\mathbf{v}^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)=\mathbf{0}\quad\text{for }\alpha\in\mathfrak{J}_{\mathrm{I}}\,. \tag{11.97}$$

It is not surprising that one obtains this condition, since the momentum of a massless entity is zero. Eq. (11.97) essentially confirms the discussion in Sect. 8.7.1 where the average normal velocity of the interface was obtained as a function of the velocities of the adjacent phases.

Momentum Conservation for the Common Curve

The momentum equation for a massless common curve in conjunction with the stress tensor given by Eq. (11.86) and the closure relation of Eq. (11.89) is

$$\hat{\mathsf{R}}^{wns}_{wns}\cdot\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)+\sum_{\kappa\in\mathfrak{J}_{\mathrm{f}}}\hat{\mathsf{R}}^{wns}_{\kappa}\cdot\left(\mathbf{v}^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)=\mathbf{0}\,. \tag{11.98}$$

This condition is similar in character to that for the interfaces. Expressions for the common curve velocity were discussed in Sect. 8.7.2. In many instances it is expected that accurate knowledge of the common curve velocity will not be important to the modeling of phase behavior. Thus, the difficulties in obtaining a good model of this velocity may not impact overall model accuracy significantly. We are not aware of any current model of two-fluid-phase flow that includes common-curve velocity. Here, we have shown explicitly how assumptions impact the entry of this velocity into the total formulation.

Momentum Conservation for the Solid Phase

The momentum for the solid phase is usually accounted for alternatively by using a momentum equation for the entire system. This equation is a summation over the fluid phase and interface momentum equations plus the solid phase. The advantage of this form is that the momentum exchange rates between entities cancel. Summing the momentum equations $\mathcal{P}^{\overline{\overline{\alpha}}}_{*}$ from Table 6.3 over all entities and eliminating terms because the interfaces and common curve are massless according to Secondary Restriction 11.3 gives

$$\sum_{\alpha\in\mathfrak{J}_{\mathrm{P}}}\left[\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}})}{\mathrm{D}t}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\right]-\sum_{\alpha\in\mathfrak{J}}\nabla\cdot\left(\epsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right)=\mathbf{0}\,. \tag{11.99}$$

Substitution of closure relations Eqs. (11.83)–(11.86) for the stress tensors then provides:

$$\sum_{\alpha\in\mathfrak{J}_{\mathrm{P}}}\left[\frac{\mathrm{D}^{\overline{\alpha}}(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}})}{\mathrm{D}t}+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\right]-\nabla\cdot\left(\epsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right)+\sum_{\alpha\in\mathfrak{J}_{\mathrm{f}}}\nabla\left(\epsilon^{\overline{\overline{\alpha}}}p^{\alpha}\right)$$

$$-\sum_{\alpha\in\mathfrak{I}_\mathrm{I}}\nabla\cdot\left[\varepsilon^{\overline{\overline{\alpha}}}\left(\mathbf{I}-\mathbf{G}^{\alpha}\right)\gamma^{\alpha}\right]+\nabla\cdot\left[\varepsilon^{\overline{\overline{wns}}}\left(\mathbf{I}-\mathbf{G}^{wns}\right)\gamma^{wns}\right]=\mathbf{0}\,. \tag{11.100}$$

The form of the solid stress tensor, $\mathbf{t}^s$, is then posed based on the material characteristics of the solid. An analysis for an elastic solid with small deformation in the presence of a single fluid was presented in Sect. 9.7.1. The analysis for the solid stress in the presence of two fluids differs only slightly.

The conservation equations obtained here in conjunction with state equations, closure relations, and approximations of variables is a closed equation set that can be solved to simulate a system. Despite this assertion, the actual implementation of a model is not straightforward. A number of coefficients appear whose values must be determined or whose functional dependences must be ascertained. This complexity should not suggest that our efforts have yielded nothing useful. Far from it! In fact, the terms and equations not traditionally encountered hint at what has been ignored in models currently in use. We will therefore proceed to show how the model set developed here can reduce to a traditional model while making explicit additional assumptions that are inherent in the model.

11.6 Simplified Momentum Equations for Example Model

In many cases of two-fluid-phase flow in a porous medium, the velocity of the flow is slow enough (i.e., Reynolds number less than 1) that the inertial terms in the momentum equations can be neglected. The assumption of slow flow does not change the forms of the phase mass conservation equations as given in Eq. (11.95). However, the momentum equations for the fluid and the solid phases do simplify. Also, the momentum equations for the interfaces and common curve are neglected so that the velocities of these entities are eliminated as a part of the model.

For conditions of slow flow with the inertial terms neglected, the fluid phase momentum equations are obtained from Eq. (11.96) as

$$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}\right)+\hat{\mathbf{R}}^{\alpha}_{w}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)+\hat{\mathbf{R}}^{\alpha}_{n}\cdot\left(\mathbf{v}^{\overline{n}}-\mathbf{v}^{\overline{s}}\right)=\mathbf{0}\quad\text{for }\alpha\in\mathfrak{I}_\mathrm{f}\,. \tag{11.101}$$

The Gibbs-Duhem equation for a multi-species fluid phase is given in Eq. (7.33). If we change the differential operator to a gradient and note that we are interested in single-species fluids at constant temperature, this equation becomes

$$-\varepsilon^{\overline{\overline{\alpha}}}\nabla p^{\alpha}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\mu^{\overline{\alpha}}-\left\langle\nabla\left(p_\alpha-p^{\alpha}\right)\right\rangle_{\Omega_\alpha,\Omega}+\left\langle\rho_\alpha\nabla\left(\mu_\alpha-\mu^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega}=\mathbf{0}$$
$$\text{for }\alpha\in\mathfrak{I}_\mathrm{f}\,. \tag{11.102}$$

When the microscale body force acceleration is related to its potential according to

$$\mathbf{g}_\alpha+\nabla\psi_\alpha=\mathbf{0}\,, \tag{11.103}$$

it is straightforward to show that multiplication of this expression by ρ_α and averaging over phase α yields

$$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}} + \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\psi^{\overline{\alpha}} + \left\langle \rho_\alpha \nabla\left(\psi_\alpha - \psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} = \mathbf{0}\,. \tag{11.104}$$

Addition of Eqs. (11.102) and (11.104) and minor rearrangement of the terms shows that

$$\begin{aligned}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}}\right) &= \varepsilon^{\overline{\overline{\alpha}}}\left(\nabla p^{\alpha} - \rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\right) + \left\langle \nabla\left(p_\alpha - p^{\alpha}\right)\right\rangle_{\Omega_\alpha,\Omega} \\ &\quad - \left\langle \rho_\alpha \nabla\left(\mu_\alpha + \psi_\alpha - \mu^{\overline{\alpha}} - \psi^{\overline{\alpha}}\right)\right\rangle_{\Omega_\alpha,\Omega} \quad \text{for } \alpha \in \mathcal{I}_{\mathrm{f}}\,.\end{aligned} \tag{11.105}$$

When the gradients in volume fractions are negligible within the averaging region and the gradients of pressure and potential deviations are also small, the last two terms of this equation may be eliminated to give

$$\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}}\right) = \varepsilon^{\overline{\overline{\alpha}}}\left(\nabla p^{\alpha} - \rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\right) \quad \text{for } \alpha \in \mathcal{I}_{\mathrm{f}}\,. \tag{11.106}$$

We emphasize that this is an approximation that may not hold, particularly when the gradients in saturation are significant. The more general form of the fluid momentum equation is Eq. (11.101), but we can make use of the approximate relation of Eq. (11.106) to revise this equation to

$$\varepsilon^{\overline{\overline{\alpha}}}\left(\nabla p^{\alpha} - \rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\right) + \hat{\mathbf{R}}^{\alpha}_{w}\cdot\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right) + \hat{\mathbf{R}}^{\alpha}_{n}\cdot\left(\mathbf{v}^{\overline{n}} - \mathbf{v}^{\overline{s}}\right) = \mathbf{0} \quad \text{for } \alpha \in \mathcal{I}_{\mathrm{f}}\,. \tag{11.107}$$

The inertial terms in Eq. (11.100), which describes conservation of the system momentum, can be eliminated to yield

$$\sum_{\alpha\in\mathcal{I}_{\mathrm{P}}} \varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}} + \nabla\cdot\mathbf{t}_T = \mathbf{0}\,, \tag{11.108}$$

where

$$\mathbf{t}_T = \varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s} - \sum_{\alpha\in\mathcal{I}_{\mathrm{f}}} \varepsilon^{\overline{\overline{\alpha}}}p^{\alpha} + \sum_{\alpha\in\mathcal{I}_{\mathrm{I}}} \varepsilon^{\overline{\overline{\alpha}}}\left(\mathbf{I} - \mathbf{G}^{\alpha}\right)\gamma^{\alpha} - \varepsilon^{\overline{\overline{wns}}}\left(\mathbf{I} - \mathbf{G}^{wns}\right)\gamma^{wns}\,. \tag{11.109}$$

Equation (11.108) is useful for modeling the solid-phase deformation.

The phase mass conservation equations given as Eq. (11.95) and the momentum conservation described by Eqs. (11.107) and (11.108) consist of 12 equations in the unknown variables

$$\begin{aligned}\mathcal{V} = \{&\varepsilon^{\overline{\overline{\alpha}}}, \rho^{\kappa}, \mathbf{v}^{\overline{\kappa}}, p^{w}, p^{n}, \mathbf{g}^{\overline{\kappa}}, \mathbf{t}^{s}, \mathbf{G}^{wn}, \mathbf{G}^{ws}, \mathbf{G}^{ns}, \mathbf{G}^{wns}, \\ &\gamma^{wn}, \gamma^{ws}, \gamma^{ns}, \gamma^{wns}\} \quad \text{for } \alpha \in \mathcal{I}, \kappa \in \mathcal{I}_{\mathrm{P}}\,.\end{aligned} \tag{11.110}$$

This set consists of 79 scalar components so that use of mass and momentum conservation leaves a deficit of 67 equations. This deficit count can be reduced by 15 because the five tensors listed are symmetric. The phase volume fractions sum to 1, providing a useful condition. Also, if the body force acceleration is specified to be gravity, the deficit count can be reduced further by nine to 42. Formulating these additional 42 conditions presents a fine challenge. The conditions that will be imposed here consist of a set of approximations that are subject to revision if they prove to be unsatisfactory.

We itemize a proposed set of approximations as follows, with the number of conditions imposed at the beginning of each item:

- (7) All quantities relating to the common curve are negligible, eliminating $\mathbf{G}^{wns}$ and γ^{wns};
- (18) The interfaces have no preferred orientation such that $\mathbf{G}^{\alpha} = \mathbf{I}/3$ for $\alpha \in \mathcal{J}_{\mathrm{I}}$;
- (3) Interfacial tensions are specified constants;
- (6) The solid-phase stress tensor is treated as in Eq. (9.102) (with p^w in that equation replaced by a weighted sum of p^w and p^n) or the solid phase is treated as being a passive phase, as in subsection 9.7.2;
- (3) Equations of state are available that express the mass densities of the phases as functions of pressure (or normal stress for the solid);
- (2) Equations for evolution of the solid-fluid interfaces as in Eq. (8.59)[5] will be employed;
- (1) An equation for evolution of the *wn* interface, such as Eq. (8.69) with the terms relating to the common curve deleted, is appropriate;
- (1) A statement about the pressure balance at the *wn* interface is employed as in Eq. (11.90) (which would also require that relations be stated between fluid pressures averaged over the interface and over the phase as well as state equations for J_w^{wn} and $\varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}$);
- (1) A statement about the force balance at the solid surface is used, such as Eq. (11.91) with the common curve terms deleted and conditions specified for the remaining terms in the equation.

Admittedly, some of these conditions are difficult to specify, for example the last one if a change in porosity takes place due to an imbalance of forces. In Eq. (11.91), the fact that some phase properties are integrated over surfaces, whereas typically those properties appear in equations as phase averages, must be addressed. On the other hand, the conditions identified do model the system behavior. If they are not considered, some aspect of the system physics is being ignored. By stating these conditions explicitly, we have identified elements of the problem that could require attention.

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[5] These equations introduce the solid surface fraction in contact with each fluid phase. This parameter is important, but is difficult to specify, sometimes being specified as the fluid saturations [2].

11.7 Immobile Solid

A problem that is commonly considered is two-fluid-phase flow when the solid is non-deformable and immobile. This case eliminates the need to model any of the solid properties. For the case of slow flow, when the inertial terms in the momentum equation are negligible, we can make use of the fluid conservation of mass equations, Eq. (11.95), and the simplified fluid momentum equations of Eq. (11.107). The list of unknowns that accompanies these eight equations is

$$\mathcal{V} = \{\varepsilon^{\overline{\overline{w}}}, \varepsilon^{\overline{\overline{n}}}, \rho^w, \rho^n, \mathbf{v}^{\overline{w}}, \mathbf{v}^{\overline{n}}, p^w, p^n, \mathbf{g}^{\overline{w}}, \mathbf{g}^{\overline{n}}\} . \tag{11.111}$$

This is a set of 18 scalar variables. Thus, the deficit in conditions necessary for a fully closed set of equations, relative to the conservation equations, is only 10. Recall that when including the solid phase, the corresponding count was 67. If the solid can be treated as fixed for a problem of interest, the mathematics is greatly simplified. If the body force acceleration is exclusively gravitational, the specification of $\mathbf{g}^{\overline{w}}$ and $\mathbf{g}^{\overline{n}}$ reduces the equation deficit from 10 to four. With $\varepsilon^{\overline{\overline{s}}}$ fixed, the relation between the fluid phase volume fractions, $\varepsilon^{\overline{\overline{w}}} = 1 - \varepsilon^{\overline{\overline{s}}} - \varepsilon^{\overline{\overline{n}}}$, provides an additional condition that reduces the deficit to three.

The three additional conditions needed are as follows:

- (2) equations of state expressing the mass densities of the fluid phases as functions of the phase pressures;
- (1) a statement about the pressure balance at the *wn* interface as in Eq. (11.90) (which would also require that relations be stated between fluid pressures averaged over the interface and over the phase as well as a state equation for J_w^{wn} and $\varepsilon_{\text{eq}}^{\overline{\overline{wn}}}$).

Because Eq. (11.90) can be a cause of difficulty, we will discuss it further. For the case of an immobile, incompressible solid, the porosity is constant so that this equation becomes

$$\frac{\partial \varepsilon^{\overline{\overline{w}}}}{\partial t} - \frac{\gamma^{wn} \hat{k}_1^{wn} \left(\varepsilon^{\overline{\overline{wn}}} - \varepsilon_{\text{eq}}^{\overline{\overline{wn}}}\right)}{\left(p_w^{wn} - p_n^{wn}\right)} = \hat{c}^{wn} \left(p_w^{wn} - p_n^{wn} - \gamma^{wn} J_w^{wn}\right) . \tag{11.112}$$

We will consider several approaches to dealing with this equation. In every approach, we will need information about the variables that do not appear in the preceding set of equations. These are the additional set: $\varepsilon^{\overline{\overline{wn}}}$, $\varepsilon_{\text{eq}}^{\overline{\overline{wn}}}$, $\gamma^{wn} J_w^{wn}$, p_w^{wn}, and p_n^{wn}. For our discussion, we will assume that p_w^{wn} and p_n^{wn} can be replaced by p^w and p^n without loss of accuracy. Equation (11.112) then becomes

$$\varepsilon \frac{\partial s^w}{\partial t} - \frac{\gamma^{wn} \hat{k}_1^{wn} \left(\varepsilon^{\overline{\overline{wn}}} - \varepsilon_{\text{eq}}^{\overline{\overline{wn}}}\right)}{\left(p^w - p^n\right)} = \hat{c}^{wn} \left(p^w - p^n + p^c\right) , \tag{11.113}$$

where s^w is the saturation such that $\varepsilon^{\overline{\overline{w}}} = s^w \varepsilon$, and $\varepsilon_{\text{eq}}^{\overline{\overline{wn}}}$ and $p^c = -\gamma^{wn} J_w^{wn}$ are approximated by state functions with

$$p^c = p^c \left(s^w, \varepsilon^{\overline{\overline{wn}}} \right) \tag{11.114}$$

and

$$\varepsilon_{\text{eq}}^{\overline{\overline{wn}}} = \varepsilon_{\text{eq}}^{\overline{\overline{wn}}} (p^w, p^n, s^w, \varepsilon^{\overline{\overline{wn}}}) \, . \tag{11.115}$$

The inclusion of $\varepsilon^{\overline{\overline{wn}}}$ also requires an additional equation, which can be based on Eq. (8.69) with no common curve properties included so that

$$\frac{\partial \varepsilon^{\overline{\overline{wn}}}}{\partial t} + \nabla \cdot \left(\varepsilon^{\overline{\overline{wn}}} \mathbf{w}^{wn} \right) - J_w^{wn} \varepsilon \frac{\partial s^w}{\partial t} - \hat{k}^{wn} \left(\varepsilon_{\text{eq}}^{\overline{\overline{wn}}} - \varepsilon^{\overline{\overline{wn}}} \right) = 0 \, , \tag{11.116}$$

where the difficulties involved in specifying $\mathbf{w}^{wn}$ have been discussed in Sect. 8.7.1 and the relation between $\hat{k}^{wn}$ and $\hat{k}_1^{wn}$ is given in Eq. (11.40). The mass and momentum conservation equations plus Eqs. (11.113)–(11.116) comprise a complete set of equations for modeling the fixed-solid system. These are the equations that should generally be investigated to determine the quality of a model. However, the interfacial area density, $\varepsilon^{\overline{\overline{wn}}}$, is a difficult quantity to determine accurately. Thus, simplifications to this model have been employed in practice that implicitly serve to bypass this complication whether or not that is physically appropriate.

The easiest model based on this equation set allows the interface and volume fraction kinematics to be very fast in comparison to the system physics. This is consistent with $\hat{c}^{wn}$ in Eq. (11.113) being very large. For this case, the pressure at the interface is treated as being balanced at all times, so that Eq. (11.113) becomes

$$p^w - p^n + p^c = 0 \, , \tag{11.117}$$

and the equation of state, Eq. (11.115), is not needed because neither ε^{wn} nor $\varepsilon_{\text{eq}}^{\overline{\overline{wn}}}$ appears in the problem. In fact, this is the most commonly used model when restricted further with $\hat{\mathbf{R}}_n^w = \hat{\mathbf{R}}_w^n = 0$ in Eq. (11.107), so that cross-coupling of the velocity is not considered to be important and p^c does not depend on $\varepsilon^{\overline{\overline{wn}}}$.

A more general case that has been given some attention occurs when $\hat{k}_1^{wn}$ is considered to be large. Physically, this implies that the interface relaxes to its equilibrium value of area faster than the volume fractions of the fluids reach their equilibrium values. Thus, the second term in Eq. (11.113) is neglected and the dynamic equation is

$$\varepsilon \frac{\partial s^w}{\partial t} = \hat{c}^{wn} \left(p^w - p^n + p^c \right) \, . \tag{11.118}$$

This model is computationally attractive because $\varepsilon^{\overline{\overline{wn}}}$ is not needed for a complete model. However, this formulation is physically deficient because the relaxation of the saturation to an equilibrium value is typically faster than the relaxation of the interfacial area density.

We see that even for the highly restricted case of two-fluid-phase flow with an immobile and incompressible solid, the equations needed to model the system provide challenges. To date, most of the challenges have unwittingly been overlooked in models that are closed but not consistent with system time and length scales or which do not include variables of importance. For a large array of situations, such as when the solid deforms, the system is non-isothermal, the flow velocities are not small, and/or the interface orientations are anisotropic, equations need to be carefully formulated and studied. The opportunities for extending the work here and for extending formulations employed in current codes to better capture the physics of various porous medium systems are plentiful. Successful accomplishment of model improvements will involve iteration on proposed theoretical formulations in concert with experimental and computational studies.

11.8 Summary

In this chapter, we have illustrated the TCAT approach for deriving macroscale models for two-fluid-phase flow. The CEI has been derived and is of archival value. The general manipulations needed to derive this CEI have been summarized, and some details of the derivation appear in Sect. C.3 of Appendix C. Those calculations are intended to assist an interested reader in full reproduction of the CEI derivation. A general SEI has been developed by applying SEI approximations. An SEI for a simpler system (i.e., for the isothermal case with no mass exchange between entities and with massless interfaces and common curve) is then obtained by applying secondary restrictions.

Models that can be derived based upon the general SEI apply to a wide range of systems. Approximations were employed to determine closed equations for a typical isothermal system. It was shown that when the solid phase is rigid, the need for approximations is greatly reduced, but the determination of all relations needed to close the equation system is still challenging. The models derived include important physical quantities at the macroscale, such as curvatures, contact angles, phase properties averaged over interfaces, and interfacial tensions, that do not appear explicitly in traditional models of two-fluid-phase flow. This is a pleasing result suggesting that TCAT analysis is able to link the microscale to the macroscale with increased fidelity compared to traditional approaches.

Both the CEI and the general SEI provide convenient entry points for extension of this work. Comparison of closed models with detailed experimental work and microscale simulations will be necessary to validate and extend the TCAT models that can be derived.

Exercises

11.1. Formulate the entropy inequality analogous to Eq. (11.4) for the case of two-fluid-phase flow including chemical species transport. You may consider all species in an entity to be at the same temperature, although entity temperatures may differ.

11.2. Show that if $\varepsilon^{\overline{\overline{n}}} = 0$ such that the problem of interest is single-phase fluid flow in a porous medium, the general SEI obtained as Eq. (11.78) reduces to Eq. (9.62). If any differences are encountered, account for them in terms of different underlying assumptions.

11.3. Suppose a solid phase is approximated as being composed of small, thin, flat diskettes whose thicknesses are all much less than their extents in the other two directions.

- **a.** Estimate $\mathbf{G}^{ss}$ if the orientation of the diskettes is random in the porous medium system.
- **b.** Estimate $\mathbf{G}^{ss}$ if the diskettes are mostly parallel to each other in the porous medium system.

11.4. For the variables listed in Eqs. (11.80)–(11.82),

- **a.** provide the count of the number of scalar elements;
- **b.** provide the count of the number of conservation equations that are available;
- **c.** provide the count of the number of closure equations that are available from Eq. (11.79);
- **d.** provide the count of the number of evolution approximations that are available to describe the system; and
- **e.** provide approximations for the variables or equations of state that can be used so that the number of equations and unknowns is the same.

11.5. The linearized closure relation Eq. (11.87) was obtained from the SEI given by Eq. (11.79) where the conditions of uniform temperature and no inter-entity mass exchange are applied. Determine the corresponding linearized closure relation that is obtained from the general SEI of Eq. (11.78) that is not restricted with regard to mass exchange and temperature.

11.6. For the case where the dynamics of saturation equilibration are much faster than equilibration of the *wn* interface shape such that

$$\left| J_w^{wn} \varepsilon \frac{\partial s^w}{\partial t} \right| << \left| \frac{\partial \varepsilon^{\overline{\overline{wn}}}}{\partial t} \right| , \tag{11.119}$$

combine Eqs. (11.113) and (11.116) to obtain an equation that describes the relaxation of $\varepsilon^{\overline{\overline{wn}}}$ to its steady state value.

References

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Chapter 12
Modeling Approach and Extensions

12.1 Overview

Previous chapters have detailed the general TCAT approach, the steps needed to build TCAT models, and the development of three specific classes of models. While considerable ground has been covered, much more remains to be accomplished in extending the models presented and in going on to other cases and problem types. The purpose of this concluding chapter is to point out a few of the many opportunities that exist for evaluation and extension of TCAT models. The set of topics discussed is not an exhaustive accounting of what remains to be accomplished, but rather is illustrative of some technical challenges and application areas where TCAT models can be developed to advantage.

Chaps. 9–11 detail examples of closed models for single-fluid-phase flow and transport and for two-fluid-phase flow in porous media. Many important applications fall within these general classes of problems. While the specific models developed were restricted, the CEI's and SEI's derived support the application of a rich hierarchy of models. Thus, opportunities for additional model development exist as particular cases described by the broad CEI's and using restricted SEI's. Some of these extensions have been discussed in the previous three chapters and are relatively straightforward; other extensions are more challenging not only in the manipulations that they involve but also in requiring a substantial amount of new analysis.

This chapter will focus on elements of TCAT analysis where additional supporting work will be useful in extending all TCAT models. These elements include the modeling process, subscale modeling, and model verification and validation. These aspects of TCAT modeling can be viewed as comprising the elements of TCAT highlighted in Fig. 12.1. In addition, we discuss several example TCAT extensions.

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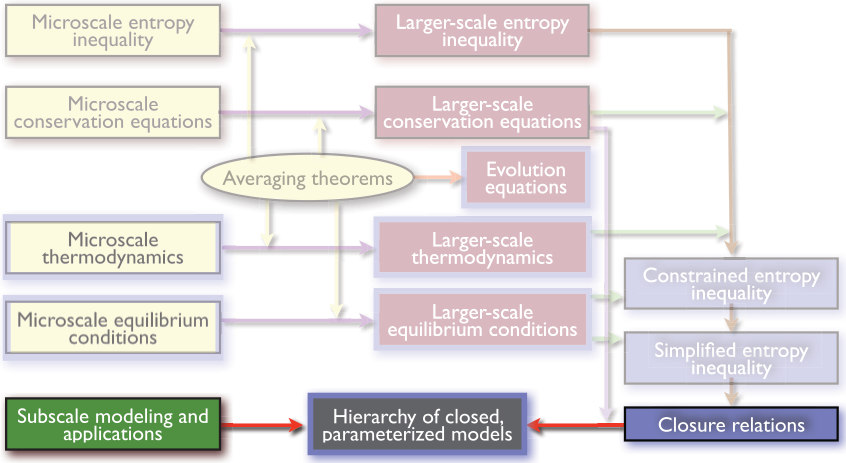

Fig. 12.1 TCAT elements of interest in Chap. 12 for model verification and validation (after [25])

12.2 Modeling Process

The TCAT approach was described in Chap. 1 and depicted graphically in Fig. 1.3. Subsequent chapters have highlighted elements of this figure in presenting the equations needed to advance useful models. Following their derivation, the components of the method have been combined to produce TCAT models for a range of systems. It has been shown that for a particular set of primary restrictions, a hierarchy of models can be developed based upon choices made for secondary restrictions, SEI approximations, and closure approximations. The general guidance given is that the sophistication of the model should be matched to the sophistication of the application that one wishes to describe. Sometimes this match will be accomplished in a direct manner. At other times an iterative procedure of model building and refinement will be required before an appropriate formulation is deduced for a problem of interest.

Because of the structure of the TCAT approach, the assumptions and approximations made in constructing a model are all explicitly stated. These include the primary restrictions used to derive a CEI, the secondary restrictions and SEI approximations used to derive an SEI, the closure approximations needed to derive the closure relations, and the approximations needed to derive the evolution equations that approximate kinematic changes in entity measures. When a TCAT model does not describe a physical system that it is intended to describe, the model formulation must be modified. Such modifications have three primary points of entry: the CEI, the SEI, and the closure relations. The effort required to revise a model is typically greatest when reformulating a CEI because a new CEI leads to a new SEI and revised closure relations. If one needs to modify only the SEI and the closure relations, the effort will be less. A modification of only the closure relations requires the least amount of mathematical work. This assessment can be seen by examining Fig. 1.3 and the flow of the work in model development.

12.2.1 On Primary Restrictions

Typically only a few primary restrictions are needed to formulate a CEI. The TCAT model builder should place special emphasis on ensuring that the primary restrictions are adequate for the class of model needed. The violation of a primary restriction will necessitate a re-derivation of the CEI, a substantial amount of work that can be avoided under most circumstances. We can elucidate why this is so.

Important aspects of the primary restrictions include the system and the scale at which the system is being modeled. Specification of these features requires that one identify and describe the entities of concern as well as the spatial dimensionality at which they will be modeled. Knowing which phases, interfaces, common curves, and common points exist in a system of interest should be straightforward if one has some familiarity with that system.

The spatial dimensionality for modeling a system requires some thought. In the applications considered in the last three chapters, systems were modeled as being macroscopic in three spatial dimensions. However, it is sometimes mathematically advantageous and physically appropriate to represent a system in terms of a mixture of macroscale and megascale dimensions. In other words, in some cases spatial variability in one or more dimensions may be considered unimportant such that a model can be simplified by averaging over this dimension. The decision to make use of a partially megascale description of system physics is important because it impacts the forms of the conservation, balance, thermodynamic and evolution equations. For example, possible formulations could treat a system at the megascale in one or more spatial dimensions while the remaining dimensions are modeled at the macroscale.

One of the primary restrictions used in the applications considered in this book required that the models derived be deterministic in nature and apply to an REV scale. On the surface, this primary restriction might appear to be tenuous for many systems of concern, since many natural systems are highly heterogeneous and are most likely stochastic as well. Such a situation might seem to preclude the use of TCAT models developed thus far and require a re-derivation of a CEI that accounts for these vagaries. On the other hand, systems do exist whose scale and homogeneity meet the REV condition. These systems can be modeled at the REV scale despite any subscale heterogeneities and stochasticity. As it happens, we can show that the REV scale for these systems is often relatively small—on the order of 10’s of grain diameters—in comparison to the scale of most heterogeneous applications. Thus, the variability can be treated as occurring at a scale above the scale for which the model is developed. A deterministic TCAT model can be used as a starting point on which a stochastic analysis can be built as needed. Stochastic analysis requires some form of macroscale model to be used as a foundation for the study of system behavior. A TCAT-based model helps assure that this underlying model is soundly developed and does not bury system physics in stochastic parameters. Thus, the primary restriction that macroscale models be formed at an REV scale is not a significant limitation.

Another common primary restriction deals with the phenomena being modeled. Specifically, issues such as whether the composition of an entity changes significantly and how this change is to be modeled arise. This was encountered in Chap. 10 where the decision was made in Primary Restriction 10.2 to use species-based mass conservation equations but entity-based momentum and energy equations. Various other approaches could be employed. For example, if the solid is inert or a species of concern is non-volatile, the composition of a multi-species gas phase could be time invariant. Alternatively, the velocity of a species could be modeled explicitly using a momentum equation rather than constitutively relative to the phase velocity. Careful thought should be given to the system being modeled so that the approach taken in formulating its CEI is sufficiently broad to encompass adequate modeling of all phenomena of interest. It may be better to have a more general model formulation than is needed when deriving the CEI. A general CEI can be simplified, but a restricted CEI can only be generalized by a new derivation. The complexity of the CEI dictates that one strive to develop a CEI that is general enough to model a problem of interest but not too general as to unnecessarily complicate the model-buliding process. This approach minimizes the mathematical manipulations needed to form a CEI, which are substantial in any case.

A final important type of primary restriction that is typically specified is the thermodynamic theory that will be used to connect the conservation equations with the entropy balance equation under near-equilibrium conditions. CIT has been used in this work because it has been found to produce models of utility for many common cases. There may be cases for which an alternative, more complex, thermodynamic theory is needed.

12.2.2 On SEI Approximations

The value of a CEI lies in its having sufficient breadth to support closure of a hierarchy of models of a given class with a range of sophistication and fidelity. Nevertheless, to complete the closure process, an SEI is needed. The SEI must be in strict force-flux form such that it is posed as a sum of products of independent fluxes and forces at the scale of interest. While the CEI is an exact expression, formulation of the SEI typically requires approximations in macroscale analysis. The SEI is formulated by restricting the more general CEI to a less complicated physical system by considering some processes to contribute negligibly to entropy production. Because an SEI follows from a CEI subject to a particular set of SEI approximations, the impact of various approximations can be investigated in the model validation process without re-deriving a CEI. It is more important to specify appropriate primary restrictions at the outset, before deriving a CEI, than to specify correct SEI approximations. The systematic TCAT approach allows one to move forward from an established result, such as a CEI, to subsequent results without having to perform a complete reformulation each time an approximation is to be examined. As with the CEI, a properly formed SEI can support the closure of a set of models of varying sophistication. One potentially interesting approach to model development is to formulate a sequence of SEI's starting from a general CEI and applying a series of secondary restrictions in turn. This set of SEI's serves as a set of entry points for model formulation depending upon the particular cases being modeled. Such an approach would not eliminate the need for model reformulation if an inappropriate SEI were used for a given application, but it would make the reformulation process more efficient.

A more subtle problem with formulation of the SEI is reliance upon approximations to produce the needed force-flux form. These approximations involve the breaking of averages of products to products of averages. Sometimes this is done directly; at other times, such as with capillary pressure in two-fluid-phase flow, products are split into leading order and fluctuation terms, which are in turn approximated. Important points to remember are that product-breaking strategies are needed, they are non-unique, and the validity of the approach taken can often be evaluated in conjunction with a reliable, sufficiently resolved microscale model. The mathematical process that must be avoided is the introduction of approximations that are a dominant source of error in the model. Optimally, approximation errors should be insignificant and verified as such. When the SEI approximation errors must be reduced, significant effort may be involved in identifying improved approximations that lead to a more satisfactory formulation.

12.2.3 On Secondary Restrictions and Closure

The aspect of the model building process that is most prone to introduction of errors, or unwarranted simplification of the model description, is the formulation of secondary restrictions and closure approximations. By the secondary restrictions, some processes are excluded from consideration that could be important. In that regard, secondary restrictions act somewhat similarly to primary restrictions in that they define the entities and processes that will be modeled. The closure approximations specify how the SEI will be used to produce a set of closure relations needed to formulate closed, solvable models. The closure relations must be consistent with the SEI in that they do not decrease entropy; but this requirement merely constrains potential forms of the constitutive, or closure, relations rather than specifying their precise optimal forms. Creative, and often iterative, approaches are needed to produce an appropriate set of constitutive relations for various processes.

Physical intuition, mathematical insight, and analytical skill are all needed to arrive at suitable constitutive forms. General guidance for a universal approach to obtaining closure relations that applies to all cases is difficult to give. Because TCAT equations at the macroscale are more complex than their microscale precursors, formulation of appropriate closure relations requires additional thought and effort. Issues that must be considered are the order of the closure approximations; whether cross-coupling is important and, if so, to which processes; the forms of the needed equations of state at the macroscale; and the values and functional dependences of model coefficients, and how these are estimated. Generalized guidance for each of these aspects of model building is incomplete now and for the foreseeable future. Typically, low-order approaches are a reasonable starting point. Coupling may be ignored in many cases, but when this is not possible it is usually not necessary to include the full set of forces for all fluxes.

Closure of TCAT models is completed at the scale of interest as constrained by the SEI and in the manner specified by the set of closure approximations. This approach assures thermodynamic consistency[1] and yields a closed system of equations. However, several issues arise that warrant further consideration. TCAT formulations can include general functional relations among equilibrium variables. The specific forms of these relations are needed to produce a solvable model, but these forms may be unknown. Closure approximations are posited to describe the dependence of a flux on some set of forces. Both the order of the dependence and the set of important forces for a particular flux are approximations, which optimally can be validated for accuracy. A TCAT model will include model parameters that will typically depend upon some set of properties of the system in some unknown manner. One could assume that model parameters must be measured for each application, but it is often possible to have reasonable parameter estimates and a good understanding of factors that affect the value of these parameters. The SEI that constrains the closure relations requires approximations, which once again are validated in optimal circumstances. Lastly, the TCAT approach provides a connection between the microscale and the macroscale physics and thermodynamics. The overall validity of a TCAT model and the fidelity of the model results across scales can be determined if a detailed microscale representation of a sufficiently large system exists.

Microscale experimentation and modeling are the primary routes used to formulate specific equations of state as explored in more detail in the following section.

12.3 Subscale Modeling

The task of properly posing and validating a TCAT model may seem onerous. It is reasonable at first blush to conclude that traditional models have distinct advantages compared to TCAT models in terms of the information needed for their construction. This is not really the case. Traditional models require closure relations, which have been developed over a period of decades based upon experimental observations and posited equation forms. If the physical dependence included explicitly in a TCAT model is not included in a traditional model, the hidden assumption is that the dependence is either not important or is accounted for implicitly within the model.

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[1] Thermodynamic consistency is asserted in some other modeling approaches but is not actually achieved. TCAT assures this consistency both between the microscale and the macroscale through averaging and at the macroscale alone through the enforcement of the SEI.

Validation is desirable for all models, but since conventional multiphase models do not include a rigorous consistency across scales, detailed comparison across scales is not generally possible. Thus a serious weakness in traditional models is that an important validation of the model form is precluded. The ability to perform an interscale validation within a TCAT framework is not a weakness but assuredly is an important strength.

As experimental and computational methods have improved over the last two decades, so too has our ability to study porous medium systems at the pore scale. These fundamental studies are used to forge a basic understanding of operative processes and phenomena. Pore-scale methods can also provide the information needed to construct and validate TCAT models as well as insights regarding parameterization of those models. Microscale modeling is an especially important tool in this regard, because it provides a means to evaluate a well-specified system in fine scale detail and to quantify a variety of variables that may be difficult to observe experimentally. In principle, microscale modeling provides a means to collect data that can be averaged to provide the missing information noted above that is needed to complete a TCAT model.

12.3.1 Capillarity Effects

We can explore briefly some of the ways in which pore-scale modeling could be used to advance and verify TCAT models. Consider the model of two-fluid-phase flow that was formulated in Chap. 11. Assume that complete microscale information of the distribution of an inert solid phase is known in a region of the porous medium. Such information might be known, for example, from high-resolution experimental observation of a study system [6, 31, 36, 40, 41, 45, 46] or from construction of an ideal system using algorithmic means [16]. Knowledge of the microscale domain occupied by the solid phase also determines the pore space morphology and topology. For a particular morphology, a microscale numerical model can be constructed that will accurately simulate two-fluid-phase flow. We will not delve into the methods needed to construct such a model as these details are not important for the current discussion. We simply state that the microscale domain can be identified and a microscale simulation code for that domain can be implemented. With these tools in hand, we are able to examine a macroscale TCAT model.

First, let us consider general functional forms of state equations involving the interfaces needed to close the two-fluid-phase flow problem described in Chap. 11. Proposed functional dependences for the equilibrium *wn* and *ws* interface densities can be stated, respectively, as

$$\varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}} = \varepsilon_{\mathrm{eq}}^{\overline{\overline{wn}}}(p^w, p^n, \varepsilon^{\overline{\overline{w}}}, \varepsilon^{\overline{\overline{s}}}, \varepsilon^{\overline{\overline{ws}}}) \tag{12.1}$$

and

$$\varepsilon_{\mathrm{eq}}^{\overline{\overline{ws}}} = \varepsilon_{\mathrm{eq}}^{\overline{\overline{ws}}}(\varepsilon^{\overline{\overline{w}}}, \varepsilon^{\overline{\overline{s}}}, \varepsilon^{\overline{\overline{wn}}}) \, , \tag{12.2}$$

where the dependences are all on equilibrium quantities. The evolution equations for $\varepsilon^{\overline{\overline{wn}}}$ and $\varepsilon^{\overline{\overline{ws}}}$ were proposed, respectively, as Eqs. (8.69) and (8.59). The curvature is proposed to be

$$J_w^{wn} = J_w^{wn}(\varepsilon^{\overline{\overline{w}}}, \varepsilon^{\overline{\overline{s}}}, \varepsilon^{\overline{\overline{wn}}}, \varepsilon^{\overline{\overline{ws}}}) \,, \tag{12.3}$$

and this expression can be considered for non-equilibrium instances since the curvature in a time-varying system might be expected to be a function of existing geometric variables that changes as those change. For example, in the very simple case of a collection of equisized spheres occupying a fraction of space, the curvature can be expressed as a function of the volume and surface area of spheres regardless of any shrinking or expansion of sphere sizes that may be occurring.

The microscale capillary pressure is a property of an interface and is defined as $p_{wn}^c = -\gamma_{wn}\nabla'\cdot\mathbf{n}_w = -\gamma_{wn}J_w$. It is important to have a macroscale measure of this property when considering two-fluid phase flow, and Eq. (12.3) provides the macroscopic curvature that can be multiplied by an average interfacial tension to give the capillary pressure. When $\varepsilon^{\overline{\overline{s}}}$, ε, J_s^{ss}, and $\varepsilon^{\overline{\overline{ss}}}$ are constant (i.e. for a solid with negligible deformation), the functional dependences indicated above may be simplified, and $\chi_s^{\overline{\overline{ws}}}$ may be used interchangeably with $\varepsilon^{\overline{\overline{ws}}}$ as an unknown variable. For instance, under these conditions, we might propose that the functional forms be stated as

$$\varepsilon_{\text{eq}}^{\overline{\overline{wn}}} = \varepsilon_{\text{eq}}^{\overline{\overline{wn}}}(p^w, p^n, s^{\overline{\overline{w}}}, \chi_s^{\overline{\overline{ws}}}) \,, \tag{12.4}$$

$$\chi_{s\,\text{eq}}^{\overline{\overline{ws}}} = \chi_{s\,\text{eq}}^{\overline{\overline{ws}}}(s^{\overline{\overline{w}}}, \varepsilon^{\overline{\overline{wn}}}) \,, \tag{12.5}$$

and

$$J_w^{wn} = J_w^{wn}(s^{\overline{\overline{w}}}, \varepsilon^{\overline{\overline{wn}}}, \chi_s^{\overline{\overline{ws}}}) \,. \tag{12.6}$$

The basic approach for determination of useful functional forms involves the simulation of a sufficient number and distribution of equilibrium states to provide a basis for proposing specific functional relations. Because the microscale details of phase morphology and topology, along with fluid pressures, exist for each point, all entity measures and curvatures can be computed for each point. These results are used to motivate a relational form. The desired result consists of computable forms, consistent with the SEI, that describe systems with some set of parameters that depend upon properties of the media and fluids. This approach provides an extension to traditional models for which the capillary pressure is proposed to be equal to a difference in reservoir pressures at the ends of an experimental cell and dependent on the fluid saturations and the history of capillarity within the cell. TCAT models suggest that interfacial areas between phases play a prominent role in effectively describing capillary pressure. Evidence exists to support the notion that inclusion of this expanded dependence will greatly reduce, or even eliminate, hysteresis in the equilibrium relations [e.g., 9, 38]. The final word is not yet written on this active area of research.

12.3.2 Testing of Approximations

Microscale modeling can also be used for other aspects of the analysis of TCAT models because TCAT retains cross-scale linkages among variables. Some specific examples are offered that support this assertion.

One of the SEI approximations employed previously involved simplifications based upon approximating averages of products as products of averages involving geometric orientation tensors. With full microscale detail available, these approximations can be carefully evaluated. As a second example, the approximations involved in deriving the kinematic equation for capillary pressure evolution given by Eq. (11.90), or one of its simplified forms, can be evaluated by examining the dynamics of the relaxation of an interface to an equilibrium configuration. Needed information is accessible from microscale modeling. In a third instance, closure approximations involve specification of the order and dependence of the set of macroscale fluxes on a set of macroscale forces. A proposed formulation can be examined through microscale modeling to see if conjugate force-flux closure is adequate for describing a system. In addition, the first-order momentum closure approximation of Eq. (11.96) for the two-fluid-phase flow case can be evaluated. As a last example, the overall quality of a two-fluid-phase flow model can be assessed by comparing TCAT and microscale models for identical physical cases. This is done by computing the microscale solution and using this solution to compute the corresponding macroscale quantities and variables. Microscale models provide many insights into material behaviors and subscale processes that have to be accounted for, on average, in testing TCAT models or any other proposed model formulation.

12.4 Macroscale Modeling

Two important aspects of any model development process are verification and validation. Validation entails determining that a set of equations provides a reasonable description of the processes of interest for a prescribed set of conditions. For example, a model might be valid for simulating small Reynolds number flow, but invalid for describing high Reynolds number flow. Some models that are valid for isothermal processes should not be used to try to describe non-isothermal processes. Verification, on the other hand, determines if the equations underlying a computational model are being solved correctly. Bugs in a code, use of time or space discretizations that introduce unacceptable error, or misuse of data within a code are obstacles to verification.

The equations that are developed via the TCAT procedure to obtain macroscale models are of no value if they cannot be validated for description of a problem or are not solved appropriately. Thus, although validation and verification are not elements of the main focus of this book, we would be remiss if we did not give them at least passing attention.

12.4.1 Model Validation

Model validation is an essential component in mechanistic model development in general, and this assertion undeniably applies to modeling based on TCAT equations as well. Because TCAT models make use of sets of restrictions and assumptions while being based on exact sets of conservation equations, approximate models necessarily result from the procedure. Because all mechanistic models require closure relations to produce solvable systems of equations, they will always be limited by some level of approximation. Closure relations account for subscale material behavior rooted in molecular effects that must be modeled in terms of variables and coefficients proffered at the scale of the model. The TCAT approach provides guidance for the selection of candidate closure relations that do not violate basic thermodynamic constraints; but these relations satisfy only a necessary, and not a sufficient, condition for establishing an applicable model. Formal validation is required.

A common approach to validation of models is to posit a model form and perform parameter estimation to bring the model and data into some level of agreement. Satisfactory agreement suggests validation is possible. However, by itself, this situation does not provide validation because agreement between a model and data does not guarantee that the underlying physics are being described mechanistically or that the model can be used when the driving forces for system dynamics change. The philosopher of science, Karl Popper, concluded that models cannot be validated, only proven invalid for a specific use [39]. This perspective has been the subject of controversy in the geosciences [e.g., 7, 32] and in other areas of scientific inquiry as well. Newton's laws of motion were viewed as universally valid until the general theory of relativity was proposed. Subsequent experimental observations confirmed Einstein's theory. The point here is that a model may describe many observations, but if that model has not been compared to all situations it is used to represent, the model is not truly validated. In practice, universal validation is rarely possible. Newton's laws are sufficiently accurate for many situations and are validly used in describing a wide range of problems. This points to the importance of matching the sophistication of a model to its intended use in answering a question of interest.

A good case in support of a model's validity can be made when the model is used successfully in predictive mode. Any model can match any data set if the model contains enough free parameters. This does not guarantee anything about the suitability of the model for studying phenomena of interest. However, if a model is used to predict behavior, and the predicted behavior is found to occur, a better case can be made that the model has a broad scope of applicability. For example, a set of TCAT equations has parameters that must be specified. If one specifies these parameters independently of the system one is endeavoring to describe and the model predictions and experimental observations for the system agree, evidence of validation exists. The more times this kind of comparison is undertaken successfully for different sorts of systems or different conditions in the same system, the more confidence one has that the model is valid for the range of operating conditions examined. In essentially all cases, some model error will occur. The practical issue is determining when a model is sufficiently accurate to answer the scientific questions being posed concerning a study system.

If one compares a model prediction to the behavior of a physical system, there can be multiple reasons that the physical data might not match the model output. Among these reasons are errors in the observed data, errors that exist in boundary or initial conditions, inaccurate values of model parameters, and inconsistent time and length scales between the system observations and the model output. Model-data comparisons must be completed carefully to identify causes of inconsistencies.

Difficulties in TCAT model-data comparisons are compounded because of the evolution of geometric variables and entity densities. These quantities are non-traditional and include orientation tensors, average curvatures, average contact angles, specific interfacial areas, and specific common curve lengths. A proper validation of a TCAT model includes comparisons of observations and model predictions for these quantities in addition to more traditional quantities, such as averaged volume fractions, fluid pressures, and fluid velocities. Modern advancements in high-resolution experimental methods make these observations and comparisons possible for certain special cases. Synchrotron-based photon attenuation methods are a class of techniques that have yielded significant results [1, 3, 12, 42, 45]. Magnetic resonance imaging is another useful method that can be employed for TCAT model validation [8].

Because variables in TCAT models have explicit connections across length scales, an additional approach for model validation can be implemented. A micromodel simulation can be performed for an ideal system in which the solid phase geometry is completely specified. Since all details of flow and transport are computed in a microscale simulation, the information generated can be used to support a TCAT model through averaging of microscale quantities. Microscale simulations can be computationally intensive due to the fine discretization necessary and the need to simulate a system of sufficient size to be macroscopically representative and suitable for validation purposes. For this approach to be of most use, the microscale simulation must be accurate, sufficiently resolved, and carried out in a domain large enough to provide a meaningful basis for comparison to a TCAT model. Pore network modeling [e.g., 4, 5, 11, 17, 18] and lattice Boltzmann methods [e.g., 16, 26, 37, 44] are two useful microscale approaches.

If a TCAT model is found to be lacking in accuracy for a given application, then the SEI restrictions and approximations must be examined and modified to obtain a more robust model. The various entry points for such reformulations were discussed in Sect. 12.2. If the original TCAT model were formulated appropriately, a complete model reformulation would generally not be needed. The model reformulation process is facilitated by the archival CEI and SEI that accompany a TCAT analysis.

The explicit list of restrictions and approximations that lead to a TCAT model, along with the possible need to validate and iteratively reformulate a model, are strengths rather than weaknesses. A clear set of opportunities exists for improving a model and resolving technical issues that hinder its utility. Validation of a traditional model may also fail. Because traditional models were not originally formulated systematically, less guidance exists for model reformulation. Also, because consistency across scales is not enforced either traditionally or in other averaged models, microscale modeling or observations are not as useful in diagnosing and minimizing potential sources of error as with TCAT models.

12.4.2 Model Verification

Model verification is a key step in the development of mechanistic models that do not in general admit analytical solutions. Model verification is also a necessary corequisite with model validation in ensuring that a TCAT model is a useful tool. Since an approximate numerical solution to TCAT model equations is typically needed, it is important that the adequacy and correctness of any numerical approximations and computer codes be established. Verification is the process whereby one endeavors to demonstrate that the formulated equations have been approximated to a useful level of accuracy. Verification does not imply that the model describes the physical system that it was originally intended to describe. While numerical approaches to approximate TCAT models fall outside the scope of this book, verification is important regardless of the approximation method used.

There are three main components to verification: code verification, input verification, and solution verification [19]. Code verification encompasses standard software quality engineering practices to eliminate coding errors. This element of verification is primarily the responsibility of code developers who may have very limited understanding of the physical problem being addressed. However, it is an important factor in establishing the predictive credibility of simulations. Input verification is intended to evaluate whether or not a model was constructed as intended. For example, questions related to correct mesh generation and appropriate boundary conditions are answered in the input verification process. Solution verification may include a grid convergence study, which provides some basis for numerical accuracy assessment, and/or studies of a model's sensitivity to inherent code parameters that affect discretization or convergence. All three types of verification are important parts of any model development process and are independent of specific data that might characterize a particular system.

A range of strategies exist for model verification. In many instances, a general model formulation may be simplified to a case for which an analytical solution either exists or may be derived by setting some parameters to zero or linearizing closure relations. A general computed solution is then compared to an analytical solution for the simplified case. This does not provide a comprehensive verification, but it is a line of evidence that an accurate solution to the more general problem may be plausibly obtained.

Since TCAT models are based upon conservation principles, an accurate numerical solution should conserve the corresponding quantities. Conservation of mass, momentum, and energy can be checked locally, for example over a small discretized region within the domain, or globally over the entire domain. The ability to conserve physical properties is a necessary, but insufficient, condition that suggests model verification. Calculation of the conservation properties of a model is straightforward and can be performed for any simulation.

An important solution verification step that can be taken with any computer code is the analysis of error as a function of discretization of the system domain. If a "true" or analytic solution does not exist, then a very high resolution approximation may be computed and used as the "exact" solution. The accuracy of a numerical approximation when the grid is coarser can then be examined to determine the rate of convergence of the calculated solution to the "exact" solution as the grid is refined. Alternative discretization approaches can be compared, and the consistency, stability, and expected analytical convergence rate can be analyzed and compared to computed results.

Together the approaches mentioned are elements of verification of a computed approximate solution to a set of TCAT model equations. The verification process must always be ongoing when a model is applied to different scenarios and situations. For example, coding errors that may not impact one case may be crucial in another case. Thus whenever engaging in modeling, one must continually question whether errors that arise are due to an invalid model or to incomplete verification.

12.5 Extensions of TCAT Models

The particular TCAT models presented in Chaps. 9–11 are a good starting point for modeling many porous medium systems of interest. Specific formulations in conjunction with approximation, verification, and validation of models still leave considerable work to be done so that these models can be effectively employed in applied simulation. The work to develop models to this point is time consuming and requires multidisciplinary collaboration among theoreticians, numerical analysts, and experimental experts. In addition to extensions of the cases provided here, many other potential TCAT extensions can be undertaken if one possesses a spirit of adventure. These extensions involve alternative approaches to the boxes in Fig. 1.3, not just the highlighted boxes in Fig 12.1. Some of the extended models involve additional operative physical processes. Others address different scales for averaging or use of different thermodynamics. In the subsections that follow, we will allude to a few of the important features that can be included in extended models.

12.5.1 Model Class Extensions: Equations

Three classes of macroscale applications were discussed in this work: single-fluid-phase flow, single-fluid-phase flow with species transport, and two-fluid-phase flow. While these classes of models allow for the simulation of many important systems, extensions are desirable for treatment of other classes of problems. In many cases, the extensions require that additional conservation equations be added to the model formulation.

For example, many two-fluid-phase problems also involve changes in composition over space and time due to reactions, exchanges between the phases, and intraphase processes. Pesticide transport, non-aqueous phase liquid transport and remediation, carbon sequestration, and nitrogen cycling in the terrestrial environment are specific instances when modeling of two-fluid-phase flow and species transport are needed. The formulation of such a model requires the identification of the set of important entities, including phases, interfaces, and a common curve. The compositional aspects require that species conservation of mass equations be written for each entity involved in compositional changes. In addition, decisions must be made concerning the overall conservation and balance equations to be employed in modeling each entity. Species momentum equations, for example, can be specified on an entity basis, necessitating that closure relations for dispersive processes be developed, or on a species basis within each entity, necessitating that species-based stress tensors be developed for each phase. This issue has been discussed, and equations have been developed, for a single-fluid-phase TCAT species transport model formulation [22]. At a very basic level, the choice between these two alternative formulations is accomplished by selection of the Lagrange multipliers in constraining the entropy inequality with conservation equations. The model is then completed through the CEI, SEI, and closure relations. Conceptually, this extension is not particularly difficult, but the mathematical manipulations and assumptions involved in obtaining a closed model are taxing. The physics accounted for have broad applicability.

A second class of TCAT model that could be developed is three-fluid-phase flow through a porous medium. Three immiscible fluids exist, for example, when non-aqueous phase liquids are transported through the unsaturated zone, in petroleum reservoirs in which a gas phase is present, and in certain cases of carbon sequestration. Three-fluid-phase flow systems are more complex than two-fluid-phase flow systems because the larger set of possible entities (15 rather than 7) requires a larger set of conservation and balance equations, increased sizes of connected entity sets, and accounting for more complex system dynamics. Physical issues such as wettability are more complex than for the two-fluid-phase flow case. Three-fluid-phase systems are also more difficult to observe experimentally and thus have been studied in less detail than two-fluid-phase systems. The TCAT procedure applied for this class of model would require significant and imaginative work on macroscale interface and common curve evolution as well as development of appropriate SEI approximations for breaking products that arise in averaging operations. The approaches taken for the two-fluid-phase flow case would be a starting point, but additional challenges to deriving a useful form must be overcome.

Another interesting class of TCAT models that could be formulated involves three-fluid-phase flow and species transport. Compositional models are more complex than flow models, and this class of transport model would confirm this general statement. A similar set of issues exist in regard to choosing the conservation equations for which compositional changes would be formulated and evolved as was discussed for the simpler compositional two-fluid-phase transport class of models.

Other physics-based extensions are possible, including cases of multiple solid phases, but the examples identified in this chapter include the primary classes of TCAT model extensions of greatest relevance and importance when the fluid phase behavior is of primary interest.

12.5.2 Mixed-scale Dimensionality: Averaging

All of the larger-scale TCAT applications considered in this text are three-dimensional macroscale models. In some cases, a particular application can be modeled with a reduced dimensionality. This is accomplished by megascale modeling in directions where accounting for variability in function values is unimportant. For example, single-fluid-phase subsurface porous medium systems are often modeled after integrating the conservation equations through the vertical direction. In TCAT vernacular, such a case is considered at the macroscale in two horizontal spatial dimensions and at the megascale in the vertical dimension.

As another example, consider the sort of experiment performed by Henry Darcy to measure permeability [14, 15]. In Darcy's experiments, saturated flow through a column was induced by imposing a head difference across the column. Darcy found that the volumetric flow per cross-sectional area was proportional to the head difference divided by the column length. Similar experiments are still conducted to determine the coefficient of proportionality, the hydraulic conductivity, of soils and sands. Because no variation in variables through the column is considered, an appropriate model for such a system is fully megascopic. Although this problem has been studied experimentally for more than 150 years, a TCAT analysis provides some insights to the approximations that are implicit in the various equations commonly referred to as Darcy's law [23].

Since consistency across scales exists with TCAT models, the goal of moving up in scale to the macroscale or megascale is to bypass modeling massive amounts of detail. A loss of information occurs with an increase in scale, but if a question being addressed does not require the finer scale details, a simpler model at the larger scale is useful. This situation is the case when one upscales from the microscale to the macroscale; it is also the case when one moves from the macroscale to the megascale or directly to the megascale from the microscale. Consider the case of single-fluid-phase flow through a porous medium. At the microscale, complete distributions of the fluid pressure, density, and velocity within the pore space are considered. At the macroscale, the average values of these quantities associated with a representative averaging region are considered; the fine scale detail is lost. At the megascale, conditions at the external boundaries, such as a flow rate or pressure distribution, are specified, but no distribution of fluid pressures, densities, or velocity within the system is resolved; macroscale detail is lost. The loss of detailed information inherent in analyses at larger scales is accompanied by a reduction in model equation complexity and, correspondingly, by a simpler computational problem. The modeler needs to decide on the appropriate balance among the precision in the information computed, the data available to support the computation, and the complexity of the computational model employed.

Larger scale TCAT models can be posed as models of mixed dimensionality, where microscale quantities are averaged up to some combination of macroscale and megascale dimensions that total three. Mixed-dimensionality models that involve one or more megascale dimensions have not been considered in this work. These models can be formulated in a manner similar to that used for the macroscale TCAT models. However, appropriate theorems are available [24] to upscale from the microscale to a mixed-scale system, thereby changing the conservation, balance, thermodynamic, and evolution equations. So while the concept of mixed-scale dimensionality is straightforward, significant theoretical work is needed to formulate TCAT models for the set of mixed scales of potential importance and utility.

12.5.3 Multiphysics: Linking of Larger-scale Systems

"Multiphysics" is a term used to describe processes in systems composed of a set of non-overlapping subdomains whose physical behavior is described by a different form of equation set in each domain. This difference arises from the modeling in each domain being at different time and/or space scales. For example, consider the problem of land-atmosphere interaction, which is of profound importance for many specific applications such as irrigation, water resources conservation, and climate change. The atmosphere can be considered as a single-fluid phase when one is not concerned with precipitation events or the dynamics of particulates. The shallow subsurface is typically a two-fluid-phase porous medium system where liquid water interacts with an air phase. The time scale of changes in the atmosphere is much shorter than that for the subsurface. The length scale of subsurface processes must take into account the impact of pore sizes, while the atmospheric flow region is homogeneous over a much larger length scale. Thus, the conservation equations for the two domains are typically posed at different scales, the closure relations in the two domains are different, and the resulting descriptions of physics are different for the two domains.

An issue for multiphysics applications is how to model the transition between regions modeled at different scales and using different equations. TCAT models can be constructed that include transition zones that act as an interface between disparate regions. To accomplish the linkage between regions, the entities in the transition zone are taken to be a union of the entities in both subdomains. Megascale averaging is performed in the dimension across the transition zone. Mass, momentum, and energy must be conserved within the transition region and for the overall system. Thus, care is needed in formulating the linkage conditions of the transition region. An example of a TCAT transition zone approach to modeling multiphysics problems is available in the context of land-atmosphere interaction [28].

The work involved with formulating a transition zone model involves the derivation of a CEI and SEI for a system with mixed dimensionality as described in

Sect. 12.5.2 and based upon the union of the entities in both regions. This transition region model will thus resemble a mixed-scale model where entity types existing in the adjacent domains are accounted for in the transition zone. An important distinguishing aspect of a model that includes a transition zone is the set of boundary conditions that link the transition region to each adjacent subdomain. Many transition region models for multiphysics applications are of interest but have yet to be completely derived and specified (e.g., a clay layer separating two aquifers, hyporheic zone hydrology). Validation of such models and comparison to traditional sharp-interface models are also promising areas for future research. We can comment that although significant attention is being devoted to computational challenges involved in multiphysics problems [30], it is ironic that far less attention is being devoted to ensuring that the equations being solved effectively describe the system.

12.5.4 Alternative Thermodynamic Theories

TCAT approaches for building larger scale models rely upon a microscale thermodynamic theory that is selected and specified in a primary restriction. The thermodynamic theory is stated in a primary restriction because of the central role that this choice has in the formulation of the CEI. TCAT relies upon careful averaging of microscale thermodynamics to the macroscale and derivation of a set of dynamic near-equilibrium equations for each entity. The purpose of these thermodynamic equations is to provide the means to connect the system entropy inequality to the conservation equations.

For the TCAT models derived in this work, classical irreversible thermodynamics (CIT) was used. This formulation is the simplest thermodynamic theory that can be employed. It makes use of the microscale local equilibrium assumption, which asserts that the equilibrium thermodynamic relations that can be formulated take on the same functional form locally even when the thermodynamic functions depend on space and time. After averaging, a macroscale local equilibrium assumption is not required, but accounting effectively for the absence of this constraint presents some theoretical challenges. Additionally, we assumed that the solid-phase deformations were small and elastic. Extension of TCAT modeling to include plastic and viscoplastic materials has not been investigated to date.

In some instances, for example when a system is far from equilibrium, CIT may not provide an adequate thermodynamic basis. Some other, more general, thermodynamic formalisms were mentioned in Sect. 3.12 and are discussed in more detail elsewhere [21, 29, 33]. Although some elements of these thermodynamic extensions have been employed in deriving larger scale models of porous medium systems, they have not been averaged from the microscale. When these thermodynamic theories are posed directly at the macroscale [e.g., rational thermodynamics 2, 20, 27] the subscale variations in thermodynamic variables are implicitly ignored, and the variables that result can be undefined and lack a relation to classically defined microscale variables [25].

While CIT has proven useful for TCAT models considered to date, it is important to be aware that alternative approaches to thermodynamics exist. If validation of a TCAT model is found to be impossible within the CIT framework, the system is far removed from equilibrium, and other approximations are found to be reasonable, a model reformulation that could be more flexible and of higher fidelity may be possible making use of one of the extended thermodynamic formalisms.

12.5.5 Nonlinearities: Closure Relations

When a system makes use of nonlinear state equations for microscale modeling, this can pose challenges to TCAT modeling and closure at larger scales. For example, consider a typical microscale equation of state for a fluid in which density depends exponentially on a deviation in fluid pressure from a reference pressure. Because TCAT models are averaged about some representative averaging region, the relation between macroscale average pressure and the macroscale average density may not satisfy the same functional form. Thus, a modified equation of state in terms of larger scale variables may be needed. The error involved in using larger scale variables in a microscale equation of state functional form is related to the size of the difference between a microscale variable and its larger scale counterpart. Thus, when the gradient in pressure is large, the use of a microscale equation of state form at the macroscale may not be satisfactory. The length scale of an averaging region can vary from tens of grain diameters in macroscale averaging to a characteristic length of the system for megascale averaging. As the size of the averaging region becomes large, the impact of deviations between microscale variables and their larger scale values becomes more important. This problem can be addressed by seeking alternative forms of an equation of state that reduces to the microscale form when the averaging region is small or gradients within the averaging region are negligible. Larger scale measures of the deviation of the equation from the microscale form can be used to suggest alterations to the equation.

Another situation in which nonlinearities pose a challenge is when modeling chemical reactions that depend nonlinearly on some combination of chemical potentials or mass fractions, as discussed briefly in Sect. 10.10.1. The reason for the difficulty is similar to that discussed above for the nonlinear equation of state. Assume the chemical mechanism and rate coefficients are known for a well-mixed system. Using this information directly as a closure relation over a representative averaging region assumes that the reactants are uniformly distributed within the averaging region. When this is not the case, error will result. An extreme example is the case of a binary reaction for which the two reactants are segregated within the averaging region. Although both reactants have non-zero averaged concentrations, no reaction will occur because microscopically the chemicals do not interact. Thus use of the known microscale reaction formula making use of average concentrations will overestimate the effective reaction rate. In considering this situation, one can see that if the differences between point and average values of reactants are small, the error in predicting reaction rates will be small. However, when the deviations are of the same order as the reactant concentrations, large errors result. The impact of upscaling on precipitation-dissolution reactions is particularly susceptible to modeling errors due to subscale concentration fluctuations. In these cases, increased accuracy will result as the numerical grid becomes more highly resolvedl; but averaging alone will impact the ability to use a microscale reaction rate expression to advantage. Subgrid-scale information or alternative closure relations are required to produce useful simulations in many cases. Successful formulations for chemical reactions are elusive in all modeling efforts that make use of larger scale variables, including TCAT.

12.5.6 Applications: Dynamically Coupled Multiscale Systems

In some situations, averaging-based approaches alone may not yield a model with sufficient fidelity. For example, consider the cases mentioned in Sect. 12.5.5. If efforts to estimate the fluctuation terms yield forms lacking in the necessary accuracy, alternative approaches might be needed. The most extreme of these approaches would be a dynamically-coupled multiscale approach in which a larger scale model is coupled to a model that resolves features at a scale beneath the larger scale. At first blush, this formulation would seem to be a bad idea since it appears to require more work than just solving the microscale model with no additional information. This would be so if the microscale model were solved over the entire domain. However, if troublesome regions occupy only a limited portion of the problem domain, limiting dynamic coupling to those regions may be a useful way to improve overall model accuracy with only a modest increase in computational time and effort.

As an example, consider the binary reaction case mentioned above. If two species react to produce a third species, and that reaction is fast relative to other processes, sharp gradients of the chemical constituents will develop around the reaction zone. Reaction will occur only at such an interfacial region, and a microscale model will be needed to resolve it. Portions of the domain where only one of the reactants is present would not need to be resolved at the microscale. Thus, selective and localized dynamic coupling could be done in this case. Other instances where processes are restricted to occur in a small subregion of an entire domain can be envisioned. These problems might benefit from a dynamically coupled multiscale approach, a procedure that has not yet been undertaken using TCAT methods but which offers fertile ground for future study.

12.5.7 Subscale Modeling and Applications: Stochastic Systems

Even macroscale properties of natural porous medium systems are often highly heterogeneous. This variability is manifested in parameters, such as hydraulic conductivity and dispersivity, that vary in space over relatively short length scales. Small-length-scale variability has profound effects on system behavior [e.g., 10, 13, 34, 35, 43]. Because of the well-documented dominant effects of medium heterogeneity on transport phenomena in porous medium systems, some suggest that all natural systems are actually stochastic and that deterministic models are of limited utility. Such a perspective has led to comments that TCAT models are of limited use because they are basically deterministic.

It is important to realize that stochastic models represent uncertainty in a system in a probabilistic manner. This uncertainty can be due to model parameters, initial conditions, or boundary conditions. In the limit of complete certainty, a stochastic model reduces to a deterministic model. If a stochastic model is to serve as an accurate representation of an uncertain system, then the underlying mechanistic model on which the stochastic model is built should adequately represent the mechanisms that are important. In other words, the mechanistic model serves as the foundation for a solution while stochastic considerations build on this foundation by accounting for uncertainty in the model elements. TCAT models serve as a strong foundation, and sources of uncertainty can be built on TCAT models just as they have been built on traditional deterministic models that have a much weaker physical basis. Substantial opportunities exist for addressing important questions by building stochastic models on high-fidelity TCAT modeling frameworks in a symbiotic fashion.

12.6 Summary

In this chapter we have reviewed the TCAT modeling approach with an eye toward potential extensions to the work presented in this book. The modeling process was discussed and the restrictions and approximations necessary to produce closed, solvable models were highlighted. Guidance was given to minimize the effort required to reformulate a TCAT model if model validation proves unsuccessful. The important role of subscale processes in TCAT model development was discussed, and the example of closure relations for two-fluid-phase flow was used to illuminate the problem. Elements of model validation were identified and guidance was given as to how TCAT models can be validated.

TCAT models may be extended based on the fundamental elements presented in this book to account for a variety of situations. Several examples of general classes of problems were given in this chapter. These extensions include:

- new classes of models not yet developed, including three-fluid-phase flow and transport;
- mixtures of macroscale and megascale dimensions, or mixed-scale dimensionality;
- multiphysics applications that involve joining of subdomains that are modeled using different equation forms;
- generalized thermodynamic formulations that improve fidelity in modeling systems far removed from equilibrium;

- highly nonlinear systems and systems that require dynamic multiscale coupling; and
- the use of stochastic modeling built on sound, physically-based deterministic models.

In conclusion, although the elements of the TCAT procedure for systematically developing larger scale models are well-established, this framework can find its full potential by working in concert with other computational and theoretical analysis methods to address problems of increasing complexity and importance to society. Thus, the contents of this book should be viewed best merely as an introduction to TCAT modeling.

Exercises

Based on the content of this chapter, suggested “exercises” follow directly. However, these “exercises” are more appropriate as research projects of significant complexity and long duration. To list them as “exercises” would make light of the depth of work required if one is to make progress in accomplishing any of the suggested extensions. Thus, we recommend that those interested in pursuing the scientific issues associated with any of the extensions become well-acquainted with current literature related to the problem of interest with an eye toward selecting opportunities for using TCAT to advantage.

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Appendix A
Considerations on Calculus of Variations

A.1 Fundamentals of Variational Approaches

The purpose of this section is to introduce the fundamentals of variational analysis needed to evaluate the expressions of the general form introduced in Sect. 4.4. Courant and Hilbert [2] define the task of analysis by variational methods by stating:

> In a given domain of admissible argument functions, find an argument function (or functions) of a given functional for which the latter is an extremum with respect to all argument functions of the domain lying in a sufficiently small neighborhood of the extremal argument function.

If the functional involves parameters in addition to the functions, these must be determined as well. A functional is a function that depends upon a function. In variational methods, the quantity of concern for which a maximum or minimum is sought is the integral of the functional over some domain.

For the applications at hand, we wish to determine conditions that minimize the equilibrium energy of a system as obtained from integration of the components of the total energy over the domain. The integral of concern can be written abstractly as

$$F = \int\limits_{\Omega} f(\mathbf{u})\, \mathrm{d}\mathfrak{r}\,, \tag{A.1}$$

where f is a functional, $\mathbf{u}$ is a vector of unknown functions, Ω is the domain, and F is the quantity that is to be minimized. The functions comprising $\mathbf{u}$ are implicitly assumed to depend upon the independent spatial variables, and the functional can depend upon parameters as well. In general, variational problems can depend upon the explicit derivatives of the functions $\mathbf{u}$ with respect to the independent variables in the system; many classical problems include such dependences [3].We have not written this more general form because the problems formulated in Sect. 4.4 do not include such dependences. The problems of interest do include multiple functions, unknown parameters, constraints, and multiple domains of various dimensions that

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are subject to change. All these elements must be considered in the variational analysis.

A.2 Classical Approach to Volume Integrals

In this section, we will consider the variation, or differential [3], of the integral functional given in Eq. (A.1) when Ω is a volume such that the integral is over three-dimensional space. The approach to be employed is based on that most often found in the literature [2–4, 7, 8]. For the general class of problems of concern, the functions comprising **u** and the independent variables **x** are considered to vary depending upon a parameter ε, which, when small, ensures that the variations are small and thus in the neighborhood of the true values. These variations are expressed in terms of transformation functions. Solving a minimization problem thus results in the determination of an extremum of an integral of the functional expressed in terms of transformations. The transformations can be written as [2]

$$\mathbf{x}^* = \mathbf{X}(\mathbf{x};\varepsilon) \tag{A.2}$$

and

$$\mathbf{u}^* = \mathbf{U}(\mathbf{x}^*;\varepsilon)\ , \tag{A.3}$$

where the superscript $*$ denotes a transformed quantity and **X** and **U** represent general sets of transformation functions, which depend upon ε. The transformations behave such that

$$\mathbf{x} = \mathbf{X}(\mathbf{x};0) \tag{A.4}$$

and

$$\mathbf{u} = \mathbf{U}(\mathbf{x};0)\ . \tag{A.5}$$

A Taylor series expansion of Eq. (A.2) around $\varepsilon = 0$ may be used to obtain $\mathbf{x}^*$ as

$$\mathbf{x}^* = \mathbf{X}(\mathbf{x};0) + \varepsilon\,\frac{\partial \mathbf{X}}{\partial \varepsilon}\bigg|_{\varepsilon=0} + \frac{\varepsilon^2}{2}\,\frac{\partial^2 \mathbf{X}}{\partial \varepsilon^2}\bigg|_{\varepsilon=0} + \dots\ . \tag{A.6}$$

Substituting Eq. (A.4) into this expression and defining

$$\Delta\mathbf{x} = \mathbf{x}^* - \mathbf{x}\ , \tag{A.7}$$

we obtain

$$\Delta\mathbf{x} = \varepsilon\,\frac{\partial \mathbf{X}}{\partial \varepsilon}\bigg|_{\varepsilon=0} + \frac{\varepsilon^2}{2}\,\frac{\partial^2 \mathbf{X}}{\partial \varepsilon^2}\bigg|_{\varepsilon=0} + \dots\ . \tag{A.8}$$

Truncation of $\Delta\mathbf{x}$ after the leading term provides the first-order variation of **x**, denoted $\delta\mathbf{x}$, such that

$$\delta\mathbf{x} = \varepsilon \left.\frac{\partial \mathbf{X}}{\partial \varepsilon}\right|_{\varepsilon=0} . \tag{A.9}$$

In other words, with reference to Eq. (A.7),

$$\Delta\mathbf{x} = \mathbf{x}^* - \mathbf{x} \sim \delta\mathbf{x} , \tag{A.10}$$

where $\sim$ denotes equality through order ε.

A Taylor series expansion of Eq. (A.3) around $\mathbf{x}$ and $\varepsilon = 0$ to obtain $\mathbf{u}^*$ then provides

$$\mathbf{u}^* = \mathbf{U}(\mathbf{x};0) + \varepsilon \left.\frac{\partial \mathbf{U}}{\partial \varepsilon}\right|_{\mathbf{x},\varepsilon=0} + (\mathbf{x}^* - \mathbf{x}) \cdot \nabla\mathbf{U}|_{\mathbf{x},\varepsilon=0} + \dots . \tag{A.11}$$

Substitute Eq. (A.5) into this expression and define $\Delta\mathbf{u}$ as

$$\Delta\mathbf{u} = \mathbf{u}^* - \mathbf{u} \tag{A.12}$$

to obtain

$$\Delta\mathbf{u} = \varepsilon \left.\frac{\partial \mathbf{U}}{\partial \varepsilon}\right|_{\mathbf{x},\varepsilon=0} + (\mathbf{x}^* - \mathbf{x}) \cdot \nabla\mathbf{U}|_{\mathbf{x},\varepsilon=0} + \dots . \tag{A.13}$$

If δ denotes the first variation, we can make the approximations that are accurate to order ε that

$$\delta\mathbf{u} \sim \Delta\mathbf{u} , \tag{A.14}$$

$$\overline{\delta}\mathbf{u} \sim \varepsilon \left.\frac{\partial \mathbf{U}}{\partial \varepsilon}\right|_{\mathbf{x},\varepsilon=0} , \tag{A.15}$$

and

$$\delta\mathbf{x}\cdot\nabla\mathbf{u} = (\mathbf{x}^* - \mathbf{x}) \cdot \nabla\mathbf{U}|_{\mathbf{x},\varepsilon=0} , \tag{A.16}$$

where $\overline{\delta}$ indicates a fixed-point variation, i.e., a variation at a fixed coordinate location due to the perturbation ε. Substitution of these relations into Eq. (A.13) provides the first-order accurate expression for the variation of $\mathbf{u}$ as

$$\delta\mathbf{u} = \overline{\delta}\mathbf{u} + \delta\mathbf{x}\cdot\nabla\mathbf{u} . \tag{A.17}$$

The increment of F is defined as

$$\Delta F = F(\mathbf{u}^*) - F(\mathbf{u}) , \tag{A.18}$$

where the arguments of F indicate that the evaluation is done for the transformed and the original states. The increment given by Eq. (A.18) can be expressed in terms of the integral definition given in Eq. (A.1) as

$$\Delta F = \int\limits_{\Omega^*} f(\mathbf{u}^*)\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} f(\mathbf{u})\,\mathrm{d}\mathfrak{r} , \tag{A.19}$$

where Ω^* is the perturbed domain of integration. This integration can be expressed in terms of the original domain by use of the jacobian, j, for coordinate change, defined as

$$j = |\nabla \mathbf{x}^*| \ , \tag{A.20}$$

such that

$$\Delta F = \int\limits_{\Omega} [f(\mathbf{u}^*)j - f(\mathbf{u})] \, \mathrm{d}\mathfrak{r}. \tag{A.21}$$

The quantity $\mathbf{x}^*$ can be restated, making use of Eq. (A.10), to obtain the first order approximation for the jacobian as

$$j \sim |\nabla (\mathbf{x} + \delta \mathbf{x})| \ . \tag{A.22}$$

Expansion of the determinant while neglecting higher order terms in $\delta \mathbf{x}$ yields

$$j \sim 1 + \nabla \cdot \delta \mathbf{x} \, . \tag{A.23}$$

Substitution of Eq. (A.23) into Eq. (A.21) to eliminate j then provides

$$\Delta F = \int\limits_{\Omega} [f(\mathbf{u}^*) - f(\mathbf{u}) + f(\mathbf{u}^*)\nabla \cdot \delta \mathbf{x}] \, \mathrm{d}\mathfrak{r} \, . \tag{A.24}$$

A Taylor expansion of $f(\mathbf{u}^*)$ around $\mathbf{u}$ gives

$$f(\mathbf{u}^*) = f(\mathbf{u}) + (\mathbf{u}^* - \mathbf{u}) \cdot \left. \frac{\partial f}{\partial \mathbf{u}} \right|_{\mathbf{u}} + \ldots \, . \tag{A.25}$$

This expression may be substituted into Eq. (A.24). Subsequently, from Eqs. (A.12) and (A.14), with higher order terms neglected, we obtain

$$\delta F = \int\limits_{\Omega} \left[\frac{\partial f(\mathbf{u})}{\partial \mathbf{u}} \cdot \delta \mathbf{u} + f(\mathbf{u}) \nabla \cdot (\delta \mathbf{x}) \right] \mathrm{d}\mathfrak{r} \, . \tag{A.26}$$

Next, we substitute Eq. (A.17) into Eq. (A.26) to eliminate $\delta \mathbf{u}$ such that

$$\delta F = \int\limits_{\Omega} \left[\frac{\partial f(\mathbf{u})}{\partial \mathbf{u}} \cdot \left(\overline{\delta} \mathbf{u} + \delta \mathbf{x} \cdot \nabla \mathbf{u} \right) + f(\mathbf{u}) \nabla \cdot (\delta \mathbf{x}) \right] \mathrm{d}\mathfrak{r} \, . \tag{A.27}$$

However, because

$$\nabla \cdot [f(\mathbf{u}) \delta \mathbf{x}] = f(\mathbf{u}) \nabla \cdot (\delta \mathbf{x}) + \frac{\partial f(\mathbf{u})}{\partial \mathbf{u}} \cdot (\delta \mathbf{x} \cdot \nabla \mathbf{u}) \ , \tag{A.28}$$

Equation (A.27) may be re-expressed as

$$\delta F = \int_{\Omega} \left\{ \frac{\partial f(\mathbf{u})}{\partial \mathbf{u}} \cdot \bar{\delta} \mathbf{u} + \nabla \cdot [f(\mathbf{u}) \delta \mathbf{x}] \right\} \mathrm{d}\mathfrak{r} \, . \tag{A.29}$$

Finally, apply the divergence theorem, Eq. (2.10), to the second term in the integrand of Eq. (A.29) to obtain the variational equation

$$\delta F = \int_{\Omega} \frac{\partial f(\mathbf{u})}{\partial \mathbf{u}} \cdot \bar{\delta} \mathbf{u} \, \mathrm{d}\mathfrak{r} + \int_{\Gamma} f(\mathbf{u}) \mathbf{n} \cdot \delta \mathbf{x} \, \mathrm{d}\mathfrak{r} \, , \tag{A.30}$$

where Γ is the surface that bounds the volume Ω, and $\mathbf{n}$ is the outward normal vector from the boundary. This expression agrees with a simpler scalar version derived elsewhere [1]. Because

$$\bar{\delta} f(\mathbf{u}) = \frac{\partial f(\mathbf{u})}{\partial \mathbf{u}} \cdot \bar{\delta} \mathbf{u} \, , \tag{A.31}$$

Equation (A.30) may be written in the equivalent form

$$\delta F = \int_{\Omega} \bar{\delta} f(\mathbf{u}) \, \mathrm{d}\mathfrak{r} + \int_{\Gamma} f(\mathbf{u}) \mathbf{n} \cdot \delta \mathbf{x} \, \mathrm{d}\mathfrak{r} \, . \tag{A.32}$$

We note that the approximations in Eqs. (A.30) and (A.32) involving neglect of higher order terms are consistent with the use of these relations to examine small perturbations around an equilibrium energy state.

A.3 Indicator Functions

The classical approach to development of variational expressions when integration is over a volume becomes more complex when the integration region is an interface or a curve. The derivation can be simplified by the use of indicator functions that identify volumes, interfaces, and curves that exist within an infinite three-dimensional space. A feature of this approach is that the indicator functions allow transformation from integrals over deforming finite volumes, interfaces, and curves to integrals over invariant infinite space [6]. When such a transformation is accomplished, the variation operator may be moved inside the integral operator directly, thus facilitating the derivation of useful variational relations [5].

Here we will briefly summarize the properties of indicator functions and their variations as well as their properties when appearing in integrands. We emphasize that the indicator functions are introduced into mathematical expressions to simplify the mathematical analysis. However, any equation resulting from such an analysis should not rely on the indicator function.

A.3.1 Universal Properties

The specific properties of indicator functions depend on whether the function is used to identify a volume, an interface, or a curve. Nevertheless, the definition of the indicator function and of its variation are common to all of these geometric regions.

We define the indicator function as

$$\Upsilon_\kappa(\mathbf{x},t) = \begin{cases} 1 & \text{for } \mathbf{x} \in \Omega_\kappa \\ 0 & \text{for } \mathbf{x} \notin \Omega_\kappa, \end{cases} \quad \text{for } \kappa \in \mathfrak{I} \;, \tag{A.33}$$

where $\mathfrak{I}$ refers to the set of entities of interest. Thus, for a system consisting of a solid phase, s, a wetting phase, w, and a non-wetting phase, n,

$$\mathfrak{I} = \{w, n, s, wn, ws, ns, wns\} \;, \tag{A.34}$$

where an index pair refers to an interface between the designated phases, and the triple index, wns, refers to the common curve where three interfaces meet. As an example of the use of an indicator function, the w phase is identified as the spatial domain where Υ_w is 1, the interface between the w and n phases is the surface domain where $\Upsilon_{wn} = 1$, and the common curve is the one-dimensional domain where $\Upsilon_{wns} = 1$. Note that the domain of an entity need not be continuous to make use of the indicator function denoting where it exists in space.

The indicator function is convenient because multiplying a functional by an indicator function eliminates the need to worry about changes on the boundary of the integration region. The integration region can be all of space. The movement of the boundary of Ω_κ, which we wish to allow, is tracked through changes in Υ_κ. The indicator function Υ_κ is different from the other functions that appear within the functional. The value of the function is fixed at either 0 or 1 and is not subject to variations. Thus the total variation of Υ_κ is zero, which can be expressed

$$\delta\Upsilon_\kappa = 0 \quad \text{for } \kappa \in \mathfrak{I} \,. \tag{A.35}$$

However, when the κ entity deforms, its associated indicator function Υ_κ can change its value from 0 to 1, or vice-versa, at some locations to account for the change in the domain that is spanned. Another way to conceptualize the use of Υ_κ is to see it as as a means to represent a mapping of the coordinate system from $\mathbf{x}$ to $\mathbf{x}^*$, somewhat similar to a jacobian. This re-mapping accounts for movement of the boundary of the domain. However, the variation of Υ_κ is zero. Based on Eq. (A.35), we can expand $\delta\Upsilon_\kappa$ according to Eq. (A.17) to obtain

$$\overline{\delta}\Upsilon_\kappa = -\delta\mathbf{x}\cdot\nabla\Upsilon_\kappa \quad \text{for } \kappa \in \mathfrak{I} \,. \tag{A.36}$$

Knowledge of the common properties of the indicator functions given as Eqs. (A.33) and (A.36), regardless of the entity type of interest, now lets us examine the transformation of integrals over the various entity types to integrals over all space, denoted as Ω_∞.

A.3.2 Integral over a Phase

Consider an integral of a function over a phase, α, such that

$$F_\alpha = \int\limits_{\Omega_\alpha} f_\alpha \, \mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,, \tag{A.37}$$

where Ω_α is the region occupied by the phase. The integral can be directly changed to an integral over all space by use of the indicator function Υ_α to obtain

$$\int\limits_{\Omega_\alpha} f_\alpha \, \mathrm{d}\mathfrak{r} = \int\limits_{\Omega_\infty} f_\alpha \Upsilon_\alpha \, \mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{P} \,. \tag{A.38}$$

It should be clear that since $\Upsilon_\alpha = 0$ outside the domain occupied by the α phase, the equality of Eq. (A.38) will hold.

A.3.3 Integral over an Interface

The integral over an interface of a function associated with that interface, $f_{\alpha\beta}$, where $\alpha\beta$ is the pair of indices identifying the adjacent phases, is expressed as

$$F_{\alpha\beta} = \int\limits_{\Omega_{\alpha\beta}} f_{\alpha\beta} \, \mathrm{d}\mathfrak{r} \quad \text{for } \alpha\beta \in \mathfrak{I}_\mathrm{I} \,. \tag{A.39}$$

Because this is an integral over a surface, it cannot be directly converted to an integral over a volume. First, if this surface is a closed surface, we designate the enclosed phase as the α phase. If it is not a closed surface, we can envision the surface as being a segment of a closed surface that bounds a phase α. In light of these considerations, we may re-express Eq. (A.39) as

$$F_{\alpha\beta} = \int\limits_{\Omega'_{\alpha\beta}} f_{\alpha\beta} \Upsilon_{\alpha\beta} \, \mathrm{d}\mathfrak{r} \,, \tag{A.40}$$

where $\Omega'_{\alpha\beta}$ is the closed surface bounding the α phase. The interior of each closed surface is designated as an α phase. This is a space where $\Upsilon_\alpha = 1$, while $\Upsilon_\alpha = 0$ outside this space. The gradient of Υ_α is zero everywhere except on the surface

$\Omega'_{\alpha\beta}$, where it behaves as a directional delta function. This delta function converts an integral over a volume to an integral over a surface. Thus we can write [6]

$$F_{\alpha\beta} = -\int\limits_{\Omega_\infty} f_{\alpha\beta}\mathbf{n}_\alpha\cdot\nabla\Upsilon_\alpha\Upsilon_{\alpha\beta}\,\mathrm{d}\mathfrak{r}\,. \tag{A.41}$$

Elimination of $F_{\alpha\beta}$ between Eqs. (A.39) and (A.41) yields

$$\int\limits_{\Omega_{\alpha\beta}} f_{\alpha\beta}\,\mathrm{d}\mathfrak{r} = -\int\limits_{\Omega_\infty} f_{\alpha\beta}\mathbf{n}_\alpha\cdot\nabla\Upsilon_\alpha\Upsilon_{\alpha\beta}\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha\beta\in\mathfrak{J}_\mathrm{I}\,. \tag{A.42}$$

The conceptualizations employed here have allowed the integral over a surface to be converted to an integral over all of three-dimensional space as given in Eq. (A.42). The conceptualizations will allow for some simpler analysis of variational expressions; and, in the end, the indicator functions will disappear from the result.

A.3.4 Integral over a Common Curve

A function associated with a common curve, denoted $f_{\alpha\beta\gamma}$ where the elements of $\alpha\beta\gamma$ denote the three phases that meet at the curve, can be integrated over that curve to give

$$F_{\alpha\beta\gamma} = \int\limits_{\Omega_{\alpha\beta\gamma}} f_{\alpha\beta\gamma}\mathrm{d}\mathfrak{r} \quad \text{for } \alpha\beta\gamma\in\mathfrak{J}_\mathrm{C}\,. \tag{A.43}$$

The task at hand is to convert this integral over the one-dimensional curve to an expression that is an integral over Ω_∞ by use of the indicator functions.

The curve of integration may be considered to be a segment of a curve completely bounding the $\alpha\beta$ interface. Thus, an indicator function for the curve may be used to identify the portion of interest and obtain

$$F_{\alpha\beta\gamma} = \int\limits_{\Omega''_{\alpha\beta\gamma}} f_{\alpha\beta\gamma}\Upsilon_{\alpha\beta\gamma}\mathrm{d}\mathfrak{r}\,, \tag{A.44}$$

where $\Omega''_{\alpha\beta\gamma}$ is the closed curve bounding the $\alpha\beta$ interface. This interface of interest is a portion of the surface bounding the α phase. Therefore, we can make use of the indicator function $\Upsilon_{\alpha\beta}$ to identify this portion of the surface. Specifically, the surface gradient of $\Upsilon_{\alpha\beta}$ will be non-zero only on the domain $\Omega''_{\alpha\beta\gamma}$ and is a directional delta function. This information can be used to convert the integral over the closed curve $\Omega''_{\alpha\beta\gamma}$ to an integral over the closed surface $\Omega'_{\alpha\beta}$ such that [6]

$$F_{\alpha\beta\gamma} = -\int_{\Omega'_{\alpha\beta}} f_{\alpha\beta\gamma} \mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta} \Upsilon_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} \,. \tag{A.45}$$

Following the same logic and procedures in going from Eq. (A.40) to Eq. (A.42), we can convert this surface integral to an integral over all space with

$$F_{\alpha\beta\gamma} = \int_{\Omega_\infty} f_{\alpha\beta\gamma} \mathbf{n}_{\alpha} \cdot \nabla \Upsilon_{\alpha} \mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta} \Upsilon_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} \,. \tag{A.46}$$

Elimination of $F_{\alpha\beta\gamma}$ between Eqs. (A.43) and (A.46) gives the useful relation for an integral over a curve transformed to an integral over all space

$$\int_{\Omega_{\alpha\beta\gamma}} f_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} = \int_{\Omega_\infty} f_{\alpha\beta\gamma} \mathbf{n}_{\alpha} \cdot \nabla \Upsilon_{\alpha} \mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta} \Upsilon_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} \quad \text{for } \alpha\beta\gamma \in \mathfrak{I}_{\mathrm{C}} \,. \tag{A.47}$$

The key results of this section are Eq. (A.36), which provides the identity that the variation of the indicator function is zero, and the three relations that convert integrals over a volume, surface, or curve to integrals over all space given, respectively, as Eqs. (A.38), (A.42), and (A.47). These equations will be employed in the next sections to reproduce the variational expression for an integral over a phase obtained using the classical approach, Eq. (A.32), as well as the variations of integrals over a surface and over a curve.

A.4 Variation of a Volume Integral

Consider the functional

$$F_{\alpha} = \int_{\Omega_\alpha} f_{\alpha}(\mathbf{u}) \, \mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{P}} \,. \tag{A.48}$$

For notational convenience, we will make dependence of f_α on $\mathbf{u}$ implicit. Converting the integral over a finite volume to an integral over all space by Eq. (A.38) and taking the variation of the resultant equality, we obtain

$$\delta F_{\alpha} = \delta \int_{\Omega_\infty} f_{\alpha} \Upsilon_{\alpha} \, \mathrm{d}\mathfrak{r} \,. \tag{A.49}$$

Because the integral is over all space, there will be no variation due to coordinate transformation, so the variation on the right may be changed to a fixed-point variation and moved inside the integral so that

$$\delta F_\alpha = \int\limits_{\Omega_\infty} \overline{\delta}\,(f_\alpha \Upsilon_\alpha)\,\mathrm{d}\mathfrak{r}\,. \tag{A.50}$$

Application of the product rule then yields

$$\delta F_\alpha = \int\limits_{\Omega_\infty} \overline{\delta} f_\alpha \Upsilon_\alpha\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_\infty} f_\alpha \overline{\delta}\Upsilon_\alpha\,\mathrm{d}\mathfrak{r}\,. \tag{A.51}$$

However, we can make use of Eq. (A.36) to replace $\overline{\delta}\Upsilon_\alpha$ so that Eq. (A.51) becomes

$$\delta F_\alpha = \int\limits_{\Omega_\infty} \overline{\delta} f_\alpha \Upsilon_\alpha\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\infty} f_\alpha \delta\mathbf{x}\cdot\nabla\Upsilon_\alpha\,\mathrm{d}\mathfrak{r}\,. \tag{A.52}$$

In this expression, the indicator function may be dropped from the first integral if the domain of integration reverts to Ω_α. The gradient of the indicator function in the second term is the directional delta function that converts this integral over a volume to an integral over the boundary of Ω_α. Thus, Eq. (A.52) becomes

$$\delta F_\alpha = \int\limits_{\Omega_\alpha} \overline{\delta} f_\alpha\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_\alpha} f_\alpha \mathbf{n}_\alpha\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{J}_{\mathrm{P}}\,. \tag{A.53}$$

This equation agrees with Eq. (A.32) that was developed by classical methods. The fixed-point variation of f_α can be expanded out according to Eq. (A.31) to obtain Eq. (A.30).

A.5 Variation of a Surface Integral

The variation of a quantity on a surface is more complicated than the variation of a quantity in a volume. The extent of a volume will change only by movement of its boundary in the normal direction. The extent of a surface can change not only because of movement of the curve bounding the surface but also by deformation of the surface itself. The curvature of an interface plays an important role in establishing equilibrium conditions of multiphase systems.

Consider the functional $F_{\alpha\beta}$ associated with an integral over the interface between the α and β phases of a multiphase system. The functional of interest is

$$F_{\alpha\beta} = \int\limits_{\Omega_{\alpha\beta}} f_{\alpha\beta}(\mathbf{u})\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha\beta \in \mathfrak{J}_{\mathrm{I}}\,, \tag{A.54}$$

where $\Omega_{\alpha\beta}$ is the interface formed where the α and β phases meet, and $f_{\alpha\beta}(\mathbf{u})$ is a functional defined over the interface that depends upon the set of functions, $\mathbf{u}$. This explicit designation of the functional dependence should be understood and will be dropped from here for conciseness.

Make use of Eq. (A.42) to convert the integral over $\Omega_{\alpha\beta}$ to an integral over Ω_∞. The variation of the resulting expression is

$$\delta F_{\alpha\beta} = -\delta \int\limits_{\Omega_\infty} f_{\alpha\beta} \mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha \Upsilon_{\alpha\beta} \, \mathrm{d}\mathfrak{r} \, . \tag{A.55}$$

Since the integration is over all of space, the variation operator can be moved inside the integral sign and the product rule applied, giving

$$\begin{aligned} \delta F_{\alpha\beta} = & -\int\limits_{\Omega_\infty} \overline{\delta} f_{\alpha\beta} \left(\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha\right) \Upsilon_{\alpha\beta} \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\infty} f_{\alpha\beta} \Upsilon_{\alpha\beta} \mathbf{n}_\alpha \cdot \nabla \left(\overline{\delta} \Upsilon_\alpha\right) \mathrm{d}\mathfrak{r} \\ & - \int\limits_{\Omega_\infty} f_{\alpha\beta} \left(\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha\right) \overline{\delta} \Upsilon_{\alpha\beta} \, \mathrm{d}\mathfrak{r} \, , \end{aligned} \tag{A.56}$$

where the variations inside the integrals are fixed-point variations since integration is over infinite space. Additionally, the fact that $\overline{\delta} \mathbf{n}_\alpha$ is orthogonal to $\nabla \Upsilon_\alpha$ has been employed. From Eq. (A.42), the first integral on the right may be returned to an integral over $\Omega_{\alpha\beta}$. Application of the product rule to the second integral then reformulates Eq. (A.56) as

$$\begin{aligned} \delta F_{\alpha\beta} = & \int\limits_{\Omega_{\alpha\beta}} \overline{\delta} f_{\alpha\beta} \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\infty} \left[\nabla \cdot \left(\mathbf{n}_\alpha f_{\alpha\beta} \Upsilon_{\alpha\beta} \overline{\delta} \Upsilon_\alpha\right) - \nabla \cdot \left(\mathbf{n}_\alpha f_{\alpha\beta} \Upsilon_{\alpha\beta}\right) \overline{\delta} \Upsilon_\alpha\right] \mathrm{d}\mathfrak{r} \\ & - \int\limits_{\Omega_\infty} f_{\alpha\beta} \left(\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha\right) \overline{\delta} \Upsilon_{\alpha\beta} \, \mathrm{d}\mathfrak{r} \, . \end{aligned} \tag{A.57}$$

The divergence theorem may be employed to change the first term in the second integral to an integral over the boundary of the infinite volume. However, the quantities of interest are zero at that location, so the term may be dropped. We then employ Eq. (A.36) to replace $\overline{\delta} \Upsilon_\alpha$ and $\overline{\delta} \Upsilon_{\alpha\beta}$. The resulting equation is

$$\begin{aligned} \delta F_{\alpha\beta} = & \int\limits_{\Omega_{\alpha\beta}} \overline{\delta} f_{\alpha\beta} \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\infty} \nabla \cdot \left(\mathbf{n}_\alpha f_{\alpha\beta} \Upsilon_{\alpha\beta}\right) \delta \mathbf{x} \cdot \nabla \Upsilon_\alpha \, \mathrm{d}\mathfrak{r} \\ & + \int\limits_{\Omega_\infty} f_{\alpha\beta} \left(\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha\right) \delta \mathbf{x} \cdot \nabla \Upsilon_{\alpha\beta} \, \mathrm{d}\mathfrak{r} \, . \end{aligned} \tag{A.58}$$

The next task is to expand the integrand of the second integral using the product rule. This gives

$$\delta F_{\alpha\beta} = \int\limits_{\Omega_{\alpha\beta}} \overline{\delta} f_{\alpha\beta}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\infty} \nabla\cdot\mathbf{n}_\alpha f_{\alpha\beta}\Upsilon_{\alpha\beta}\delta\mathbf{x}\cdot\nabla\Upsilon_\alpha\,\mathrm{d}\mathfrak{r}$$
$$- \int\limits_{\Omega_\infty} \mathbf{n}_\alpha\cdot\nabla f_{\alpha\beta}\Upsilon_{\alpha\beta}\delta\mathbf{x}\cdot\nabla\Upsilon_\alpha\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_\infty} f_{\alpha\beta}\left(\mathbf{n}_\alpha\cdot\nabla\Upsilon_\alpha\right)\delta\mathbf{x}\cdot\nabla\Upsilon_{\alpha\beta}\,\mathrm{d}\mathfrak{r}\,, \qquad \text{(A.59)}$$

where use has been made of the fact that $\mathbf{n}_\alpha$ and $\nabla\Upsilon_{\alpha\beta}$ are orthogonal. Now make use of Eq. (A.42) to convert the second and third integrals to integrals over $\Omega_{\alpha\beta}$ and of Eq. (A.47) (with $\Upsilon_{\alpha\beta\gamma} = 1$) to convert the last integral to an integral over the boundary of $\Omega_{\alpha\beta}$ denoted as $\Gamma_{\alpha\beta}$. The result, after combining the third integral with the first, is

$$\delta F_{\alpha\beta} = \int\limits_{\Omega_{\alpha\beta}} \left(\overline{\delta} f_{\alpha\beta} + \delta\mathbf{x}\cdot\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla f_{\alpha\beta}\right)\mathrm{d}\mathfrak{r}$$
$$+ \int\limits_{\Omega_{\alpha\beta}} \nabla'\cdot\mathbf{n}_\alpha f_{\alpha\beta}\mathbf{n}_\alpha\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{\alpha\beta}} f_{\alpha\beta}\mathbf{n}_{\alpha\beta}\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r}\,, \qquad \text{(A.60)}$$

where use has been made of the fact that $\nabla\cdot\mathbf{n}_\alpha = \nabla'\cdot\mathbf{n}_\alpha$. The fixed-point variation of $f_{\alpha\beta}$ on a surface, $\overline{\delta}' f_{\alpha\beta}$, defined such that the surface coordinates are fixed, is related to the spatial fixed-point variation by

$$\overline{\delta}' f_{\alpha\beta} = \overline{\delta} f_{\alpha\beta} + \delta\mathbf{x}\cdot\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla f_{\alpha\beta}\,. \qquad \text{(A.61)}$$

With this definition, Eq. (A.60) becomes

$$\delta F_{\alpha\beta} = \int\limits_{\Omega_{\alpha\beta}} \overline{\delta}' f_{\alpha\beta}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{\alpha\beta}} \nabla'\cdot\mathbf{n}_\alpha f_{\alpha\beta}\mathbf{n}_\alpha\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{\alpha\beta}} f_{\alpha\beta}\mathbf{n}_{\alpha\beta}\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha\beta \in \mathfrak{I}_{\mathrm{I}}\,. \qquad \text{(A.62)}$$

For a two-phase system, the last integral in this equation will be zero because there is no boundary of the interface, $\Gamma_{\alpha\beta}$. The presence of $\mathbf{n}_\alpha$ in this expression is somewhat clumsy in that the expression for the interface should be expressible in terms of properties of that interface. Therefore, we define the unit tensor in the surface, $\mathbf{l}'_{\alpha\beta}$, such that

$$\mathbf{l}'_{\alpha\beta} = \mathbf{l} - \mathbf{n}_\alpha\mathbf{n}_\alpha \quad \text{for } \mathbf{x} \in \Omega_{\alpha\beta}\,. \qquad \text{(A.63)}$$

Equation (A.62) may then be written

$$\delta F_{\alpha\beta} = \int\limits_{\Omega_{\alpha\beta}} \overline{\delta}' f_{\alpha\beta}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_{\alpha\beta}} f_{\alpha\beta}\nabla'\cdot\mathbf{l}'_{\alpha\beta}\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{\alpha\beta}} f_{\alpha\beta}\mathbf{n}_{\alpha\beta}\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha\beta \in \mathfrak{I}_{\mathrm{I}}\,. \qquad \text{(A.64)}$$

Here we have made use of the fact that

$$\nabla'\cdot\mathsf{l}'_{\alpha\beta} = -\nabla'\cdot(\mathsf{l}-\mathsf{l}'_{\alpha\beta}) = -\mathbf{n}_\alpha\nabla'\cdot\mathbf{n}_\alpha\ . \tag{A.65}$$

The surface fixed-point variation of $f_{\alpha\beta}$ can be expanded in terms of the vector of functions $\mathbf{u}$ in a form analogous to Eq. (A.31) with

$$\overline{\delta}' f_{\alpha\beta}(\mathbf{u}) = \frac{\partial f_{\alpha\beta}(\mathbf{u})}{\partial\mathbf{u}}\cdot\overline{\delta}'\mathbf{u}\ . \tag{A.66}$$

Use of Eq. (A.64) for variational analysis of the energy of an interface between phases is an essential analysis tool for multiphase systems. For porous media where the amount of interfacial area between phases is large, the energy associated with these interfaces can be significant.

A.6 Variation of an Integral over a Curve

The derivation of the expression for the variation of an integral over a curve is analogous to the previous derivations for volumes and surfaces, but it is complicated by the need to also make use of the indicator function for a common curve. The variational relation must take into account the changing of the curvature as it contributes to the state of the system.

The functional to be studied here is denoted $F_{\alpha\beta\gamma}$ and is considered to be associated with an integral over the curve where the α, β, and γ phases come together. Equivalently, it could be considered to be the location where the $\alpha\beta$, $\alpha\gamma$, and $\beta\gamma$ interfaces come together. The functional is expressed as

$$F_{\alpha\beta\gamma} = \int\limits_{\Omega_{\alpha\beta\gamma}} f_{\alpha\beta\gamma}(\mathbf{u})\,\mathrm{d}\mathfrak{r} \quad \text{for } \alpha\beta\gamma\in\mathfrak{I}_\mathrm{C}\ , \tag{A.67}$$

where $\Omega_{\alpha\beta\gamma}$ is the one-dimensional domain of the common curve and $f_{\alpha\beta\gamma}(\mathbf{u})$ is a functional defined on the common curve that is dependent on the set of functions, $\mathbf{u}$. As with the previous derivations, the explicit listing of $\mathbf{u}$ as an argument of $f_{\alpha\beta\gamma}$ will be suppressed for notational conciseness.

Equation (A.47) can be used to transform the integral in Eq. (A.67) over the common curve to an integral over the entire spatial domain, Ω_∞. The variation of the resulting equation is then

$$\delta F_{\alpha\beta\gamma} = \delta\int\limits_{\Omega_\infty} f_{\alpha\beta\gamma}\mathbf{n}_\alpha\cdot\nabla\Upsilon_\alpha\mathbf{n}_{\alpha\beta}\cdot\nabla\Upsilon_{\alpha\beta}\Upsilon_{\alpha\beta\gamma}\,\mathrm{d}\mathfrak{r}\ , \tag{A.68}$$

where $\alpha\beta$ designates a surface that is bounded by the extended common curve and α is a phase bounded by the extended surface $\alpha\beta$. The variation can be moved inside the integral, where it becomes a fixed-point variation, and the product rule applied, resulting in

$$\begin{aligned}\delta F_{\alpha\beta\gamma} = &\int\limits_{\Omega_\infty} \overline{\delta} f_{\alpha\beta\gamma} (\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha) \left(\mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta}\right) \Upsilon_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} \\ &+ \int\limits_{\Omega_\infty} f_{\alpha\beta\gamma} \left[\mathbf{n}_\alpha \cdot \nabla \left(\overline{\delta} \Upsilon_\alpha\right)\right] \left(\mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta}\right) \Upsilon_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} \\ &+ \int\limits_{\Omega_\infty} f_{\alpha\beta\gamma} (\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha) \left[\mathbf{n}_{\alpha\beta} \cdot \nabla \left(\overline{\delta} \Upsilon_{\alpha\beta}\right)\right] \Upsilon_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} \\ &+ \int\limits_{\Omega_\infty} f_{\alpha\beta\gamma} (\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha) \left(\mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta}\right) \overline{\delta} \Upsilon_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} \,, \end{aligned} \tag{A.69}$$

where use has been made of the fact that $\overline{\delta}\mathbf{n}_{\alpha\beta}$ is orthogonal to $\nabla\Upsilon_{\alpha\beta}$, and $\overline{\delta}\mathbf{n}_\alpha$ is orthogonal to $\nabla\Upsilon_\alpha$ such that the dot products of these respective pairs are zero. Equation (A.47) can be used to return the first integral to an integration over the common curve. Use of the product rule to rearrange the second and third integrals then gives

$$\begin{aligned}\delta F_{\alpha\beta\gamma} = &\int\limits_{\Omega_{\alpha\beta\gamma}} \overline{\delta} f_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} + \int\limits_{\Omega_\infty} \nabla \cdot \left[\mathbf{n}_\alpha f_{\alpha\beta\gamma} \overline{\delta} \Upsilon_\alpha \left(\mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta}\right) \Upsilon_{\alpha\beta\gamma}\right] \mathrm{d}\mathfrak{r} \\ &- \int\limits_{\Omega_\infty} \nabla \cdot \left[\mathbf{n}_\alpha f_{\alpha\beta\gamma} \left(\mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta}\right) \Upsilon_{\alpha\beta\gamma}\right] \overline{\delta} \Upsilon_\alpha \mathrm{d}\mathfrak{r} \\ &+ \int\limits_{\Omega_\infty} \nabla \cdot \left[\mathbf{n}_{\alpha\beta} f_{\alpha\beta\gamma} (\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha) \overline{\delta} \Upsilon_{\alpha\beta} \Upsilon_{\alpha\beta\gamma}\right] \mathrm{d}\mathfrak{r} \\ &- \int\limits_{\Omega_\infty} \nabla \cdot \left[\mathbf{n}_{\alpha\beta} f_{\alpha\beta\gamma} (\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha) \Upsilon_{\alpha\beta\gamma}\right] \overline{\delta} \Upsilon_{\alpha\beta} \mathrm{d}\mathfrak{r} \\ &+ \int\limits_{\Omega_\infty} f_{\alpha\beta\gamma} (\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha) \left(\mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta}\right) \overline{\delta} \Upsilon_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} \,. \end{aligned} \tag{A.70}$$

Application of the divergence theorem to the second and fourth integrals of this equation changes the integration domain from Ω_∞ to Γ_∞. The integrands are zero at this location, so these integrals must be zero. Subsequent elimination of the fixed-point variations of the indicator functions using Eq. (A.36) leaves

$$\begin{aligned}\delta F_{\alpha\beta\gamma} = &\int\limits_{\Omega_{\alpha\beta\gamma}} \overline{\delta} f_{\alpha\beta\gamma} \mathrm{d}\mathfrak{r} + \int\limits_{\Omega_\infty} \nabla \cdot \left[\mathbf{n}_\alpha f_{\alpha\beta\gamma} \left(\mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta}\right) \Upsilon_{\alpha\beta\gamma}\right] \delta\mathbf{x} \cdot \nabla \Upsilon_\alpha \mathrm{d}\mathfrak{r} \\ &+ \int\limits_{\Omega_\infty} \nabla \cdot \left[\mathbf{n}_{\alpha\beta} f_{\alpha\beta\gamma} (\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha) \Upsilon_{\alpha\beta\gamma}\right] \delta\mathbf{x} \cdot \nabla \Upsilon_{\alpha\beta} \mathrm{d}\mathfrak{r} \end{aligned}$$

$$-\int\limits_{\Omega_\infty} f_{\alpha\beta\gamma}\left(\mathbf{n}_\alpha\cdot\nabla\Upsilon_\alpha\right)\left(\mathbf{n}_{\alpha\beta}\cdot\nabla\Upsilon_{\alpha\beta}\right)\delta\mathbf{x}\cdot\nabla\Upsilon_{\alpha\beta\gamma}\,\mathrm{d}\mathfrak{r}\,. \tag{A.71}$$

It is left as an exercise in the spirit of Sects. A.3.2 through A.3.4 to show that the last integral in Eq. (A.71) can be converted from an integral over all space to a sum of evaluations at the common points at the ends of the common curve with

$$\begin{aligned}\sum_{m\in\mathfrak{I}_{\Gamma_{\alpha\beta\gamma}}}&\left(f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta\gamma}\cdot\delta\mathbf{x}\right)\big|_{\Gamma_{\alpha\beta\gamma_m}}\\ &=-\int\limits_{\Omega_\infty} f_{\alpha\beta\gamma}\left(\mathbf{n}_\alpha\cdot\nabla\Upsilon_\alpha\right)\left(\mathbf{n}_{\alpha\beta}\cdot\nabla\Upsilon_{\alpha\beta}\right)\delta\mathbf{x}\cdot\nabla\Upsilon_{\alpha\beta\gamma}\,\mathrm{d}\mathfrak{r}\,,\end{aligned} \tag{A.72}$$

where $\mathfrak{I}_{\Gamma_{\alpha\beta\gamma}}$ is the set of end points of the $\alpha\beta\gamma$ common curve, $\mathbf{n}_{\alpha\beta\gamma}$ is the unit normal outward from the end of the common curve, and m is a common point qualifier such that the summation is over all the points at the ends of the common curve segments being considered. The product rule may now be used to expand out the second and third integrals in Eq. (A.71). Some terms will be zero because the gradient of the indicator function is orthogonal to the vector it is dotted with. Other integrals will be analogous to the right side of Eq. (A.47) and thus may be transformed back to integrals over the common curve of interest. The equation simplified in this manner is

$$\begin{aligned}\delta F_{\alpha\beta\gamma}=&\int\limits_{\Omega_{\alpha\beta\gamma}}\overline{\delta}f_{\alpha\beta\gamma}\,\mathrm{d}\mathfrak{r}+\int\limits_{\Omega_{\alpha\beta\gamma}}\left(\nabla\cdot\mathbf{n}_\alpha\right)f_{\alpha\beta\gamma}\mathbf{n}_\alpha\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r}+\int\limits_{\Omega_{\alpha\beta\gamma}}\left(\mathbf{n}_\alpha\cdot\nabla f_{\alpha\beta\gamma}\right)\mathbf{n}_\alpha\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r}\\ &+\int\limits_{\Omega_\infty} f_{\alpha\beta\gamma}\left(\mathbf{n}_{\alpha\beta}\mathbf{n}_\alpha{:}\nabla\nabla\Upsilon_{\alpha\beta}\right)\Upsilon_{\alpha\beta\gamma}\delta\mathbf{x}\cdot\nabla\Upsilon_\alpha\,\mathrm{d}\mathfrak{r}\\ &+\int\limits_{\Omega_{\alpha\beta\gamma}}\left(\nabla\cdot\mathbf{n}_{\alpha\beta}\right)f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta}\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r}+\int\limits_{\Omega_{\alpha\beta\gamma}}\left(\mathbf{n}_{\alpha\beta}\cdot\nabla f_{\alpha\beta\gamma}\right)\mathbf{n}_{\alpha\beta}\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r}\\ &+\int\limits_{\Omega_\infty} f_{\alpha\beta\gamma}\left(\mathbf{n}_\alpha\mathbf{n}_{\alpha\beta}{:}\nabla\nabla\Upsilon_\alpha\right)\Upsilon_{\alpha\beta\gamma}\delta\mathbf{x}\cdot\nabla\Upsilon_{\alpha\beta}\,\mathrm{d}\mathfrak{r}\\ &+\sum_{m\in\mathfrak{I}_{\Gamma_{\alpha\beta\gamma}}}\left(f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta\gamma}\cdot\delta\mathbf{x}\right)\big|_{\Gamma_{\alpha\beta\gamma_m}}\,.\end{aligned} \tag{A.73}$$

The product rule dictates that

$$\mathbf{n}_{\alpha\beta}\mathbf{n}_\alpha{:}\nabla\nabla\Upsilon_{\alpha\beta}=\mathbf{n}_{\alpha\beta}\cdot\nabla\left(\mathbf{n}_\alpha\cdot\nabla\Upsilon_{\alpha\beta}\right)-\mathbf{n}_{\alpha\beta}\cdot\nabla\mathbf{n}_\alpha\cdot\nabla\Upsilon_{\alpha\beta}\,, \tag{A.74}$$

but the first term on the right is zero because $\mathbf{n}_\alpha$ is orthogonal to $\nabla\Upsilon_{\alpha\beta}$. Likewise, it follows that

$$\mathbf{n}_\alpha\mathbf{n}_{\alpha\beta}{:}\nabla\nabla\Upsilon_\alpha=-\mathbf{n}_\alpha\cdot\nabla\mathbf{n}_{\alpha\beta}\cdot\nabla\Upsilon_\alpha\,. \tag{A.75}$$

Substitution of these last two relations into Eq. (A.73) restates the two integrals over Ω_∞ in forms that can make use of Eq. (A.47) to convert them back to integrals over $\Omega_{\alpha\beta\gamma}$. The result of these manipulations is

$$\begin{aligned}
\delta F_{\alpha\beta\gamma} = & \int\limits_{\Omega_{\alpha\beta\gamma}} \overline{\delta} f_{\alpha\beta\gamma}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{\alpha\beta\gamma}} (\nabla\cdot\mathbf{n}_\alpha)\, f_{\alpha\beta\gamma}\mathbf{n}_\alpha\cdot\boldsymbol{\delta}\mathbf{x}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{\alpha\beta\gamma}} \left(\mathbf{n}_\alpha\cdot\nabla f_{\alpha\beta\gamma}\right)\mathbf{n}_\alpha\cdot\boldsymbol{\delta}\mathbf{x}\,\mathrm{d}\mathfrak{r} \\
& - \int\limits_{\Omega_{\alpha\beta\gamma}} f_{\alpha\beta\gamma}\left(\mathbf{n}_{\alpha\beta}\cdot\nabla\mathbf{n}_\alpha\cdot\mathbf{n}_{\alpha\beta}\right)\mathbf{n}_\alpha\cdot\boldsymbol{\delta}\mathbf{x}\,\mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Omega_{\alpha\beta\gamma}} \left(\nabla\cdot\mathbf{n}_{\alpha\beta}\right) f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta}\cdot\boldsymbol{\delta}\mathbf{x}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{\alpha\beta\gamma}} \left(\mathbf{n}_{\alpha\beta}\cdot\nabla f_{\alpha\beta\gamma}\right)\mathbf{n}_{\alpha\beta}\cdot\boldsymbol{\delta}\mathbf{x}\,\mathrm{d}\mathfrak{r} \\
& - \int\limits_{\Omega_{\alpha\beta\gamma}} f_{\alpha\beta\gamma}\left(\mathbf{n}_\alpha\cdot\nabla\mathbf{n}_{\alpha\beta}\cdot\mathbf{n}_\alpha\right)\mathbf{n}_{\alpha\beta}\cdot\boldsymbol{\delta}\mathbf{x}\,\mathrm{d}\mathfrak{r} + \sum_{m\in\mathfrak{J}_{\Gamma_{\alpha\beta\gamma}}} \left(f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta\gamma}\cdot\boldsymbol{\delta}\mathbf{x}\right)\Big|_{\Gamma_{\alpha\beta\gamma_m}} .
\end{aligned} \tag{A.76}$$

Collection of similar terms then provides

$$\begin{aligned}
\delta F_{\alpha\beta\gamma} = & \int\limits_{\Omega_{\alpha\beta\gamma}} \left(\overline{\delta} f_{\alpha\beta\gamma} + \boldsymbol{\delta}\mathbf{x}\cdot\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla f_{\alpha\beta\gamma} + \boldsymbol{\delta}\mathbf{x}\cdot\mathbf{n}_{\alpha\beta}\mathbf{n}_{\alpha\beta}\cdot\nabla f_{\alpha\beta\gamma}\right)\mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Omega_{\alpha\beta\gamma}} \left(\nabla\cdot\mathbf{n}_\alpha - \mathbf{n}_{\alpha\beta}\cdot\nabla\mathbf{n}_\alpha\cdot\mathbf{n}_{\alpha\beta}\right) f_{\alpha\beta\gamma}\mathbf{n}_\alpha\cdot\boldsymbol{\delta}\mathbf{x}\,\mathrm{d}\mathfrak{r} \\
& + \int\limits_{\Omega_{\alpha\beta\gamma}} \left(\nabla\cdot\mathbf{n}_{\alpha\beta} - \mathbf{n}_\alpha\cdot\nabla\mathbf{n}_{\alpha\beta}\cdot\mathbf{n}_\alpha\right) f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta}\cdot\boldsymbol{\delta}\mathbf{x}\,\mathrm{d}\mathfrak{r} \\
& + \sum_{m\in\mathfrak{J}_{\Gamma_{\alpha\beta\gamma}}} \left(f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta\gamma}\cdot\boldsymbol{\delta}\mathbf{x}\right)\Big|_{\Gamma_{\alpha\beta\gamma_m}} .
\end{aligned} \tag{A.77}$$

Equation (A.77) can be simplified further. The quantity in parentheses in the first integral is a variation of $f_{\alpha\beta\gamma}$ at a point fixed to the curve. We denote this fixed-point variation as $\overline{\delta}'' f_{\alpha\beta\gamma}$ with

$$\overline{\delta}'' f_{\alpha\beta\gamma} = \overline{\delta} f_{\alpha\beta\gamma} + \boldsymbol{\delta}\mathbf{x}\cdot\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\nabla f_{\alpha\beta\gamma} + \boldsymbol{\delta}\mathbf{x}\cdot\mathbf{n}_{\alpha\beta}\mathbf{n}_{\alpha\beta}\cdot\nabla f_{\alpha\beta\gamma} . \tag{A.78}$$

Also consider that

$$\nabla\cdot\mathbf{n}_\alpha - \mathbf{n}_{\alpha\beta}\cdot\nabla\mathbf{n}_\alpha\cdot\mathbf{n}_{\alpha\beta} = \mathbf{l}_{\alpha\beta\gamma}\cdot\nabla\mathbf{n}_\alpha\cdot\mathbf{l}_{\alpha\beta\gamma} = -\mathbf{l}_{\alpha\beta\gamma}\cdot\nabla\mathbf{l}_{\alpha\beta\gamma}\cdot\mathbf{n}_\alpha \tag{A.79}$$

and

$$\nabla\cdot\mathbf{n}_{\alpha\beta} - \mathbf{n}_\alpha\cdot\nabla\mathbf{n}_{\alpha\beta}\cdot\mathbf{n}_\alpha = \mathbf{l}_{\alpha\beta\gamma}\cdot\nabla\mathbf{n}_{\alpha\beta}\cdot\mathbf{l}_{\alpha\beta\gamma} = -\mathbf{l}_{\alpha\beta\gamma}\cdot\nabla\mathbf{l}_{\alpha\beta\gamma}\cdot\mathbf{n}_{\alpha\beta} . \tag{A.80}$$

Substituting these last three identities into Eq. (A.77) and collecting the expressions in the second and third integrals yields

$$\begin{aligned}\delta F_{\alpha\beta\gamma} = &\int\limits_{\Omega_{\alpha\beta\gamma}} \overline{\delta}'' f_{\alpha\beta\gamma}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_{\alpha\beta\gamma}} f_{\alpha\beta\gamma}\mathbf{l}_{\alpha\beta\gamma}\cdot\nabla\mathbf{l}_{\alpha\beta\gamma}\cdot\left(\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}+\mathbf{n}_{\alpha\beta}\mathbf{n}_{\alpha\beta}\right)\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r}\\ &+ \sum_{m\in\mathfrak{J}_{\Gamma_{\alpha\beta\gamma}}} \left(f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta\gamma}\cdot\delta\mathbf{x}\right)\big|_{\Gamma_{\alpha\beta\gamma m}} .\end{aligned} \tag{A.81}$$

Finally, we define the tensor consisting of the non-zero elements of the unit tensor that is tangent to the common curve as

$$\mathbf{I}''_{\alpha\beta\gamma} = \mathbf{I} - \mathbf{n}_{\alpha}\mathbf{n}_{\alpha} - \mathbf{n}_{\alpha\beta}\mathbf{n}_{\alpha\beta} \ , \tag{A.82}$$

so that

$$\mathbf{l}_{\alpha\beta\gamma}\cdot\nabla\mathbf{l}_{\alpha\beta\gamma}\cdot\left(\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}+\mathbf{n}_{\alpha\beta}\mathbf{n}_{\alpha\beta}\right) = \mathbf{l}_{\alpha\beta\gamma}\cdot\nabla''\mathbf{l}_{\alpha\beta\gamma}\cdot\left(\mathbf{I}-\mathbf{I}''_{\alpha\beta\gamma}\right) = \nabla''\cdot\mathbf{I}''_{\alpha\beta\gamma} \ , \tag{A.83}$$

where $\nabla'' = \mathbf{l}_{\alpha\beta\gamma}\mathbf{l}_{\alpha\beta\gamma}\cdot\nabla$ is the gradient operator along the curve. Therefore, the expression for the variation of a functional that is the integral over a curve is

$$\begin{aligned}\delta F_{\alpha\beta\gamma} = &\int\limits_{\Omega_{\alpha\beta\gamma}} \overline{\delta}'' f_{\alpha\beta\gamma}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_{\alpha\beta\gamma}} f_{\alpha\beta\gamma}\nabla''\cdot\mathbf{I}''_{\alpha\beta\gamma}\cdot\delta\mathbf{x}\,\mathrm{d}\mathfrak{r}\\ &+ \sum_{m\in\mathfrak{J}_{\Gamma_{\alpha\beta\gamma}}} \left(f_{\alpha\beta\gamma}\mathbf{n}_{\alpha\beta\gamma}\cdot\delta\mathbf{x}\right)\big|_{\Gamma_{\alpha\beta\gamma m}} \quad \text{for } \alpha\beta\gamma\in\mathfrak{J}_{\mathrm{C}} \ .\end{aligned} \tag{A.84}$$

As with the fixed-point variation for a volume property given by Eq. (A.31) and the fixed-point variation for a surface property in Eq. (A.66), an expansion for the fixed-point variation of a property of a curve may be employed with

$$\overline{\delta}'' f_{\alpha\beta\gamma}(\mathbf{u}) = \frac{\partial f_{\alpha\beta\gamma}(\mathbf{u})}{\partial\mathbf{u}}\cdot\overline{\delta}''\mathbf{u} \ . \tag{A.85}$$

Equation (A.84) will be employed in the study of three-phase systems for the variation of the energy of an interface. Note, however, that for systems composed of three phases or less, there are no common points. Thus, in these systems the summation term will not be needed.

A.7 Summary

In this appendix, it has been convenient to use single, double, and triple index notation to designate quantities related to volumes, surfaces, and curves, respectively. In the end, after all the indicator functions have been eliminated from the final expressions, we can conveniently denote the three primary results, Eqs. (A.53), (A.62), and (A.84), respectively, using single index notation as

$$\delta F_\alpha = \int\limits_{\Omega_\alpha} \overline{\delta}^{(n)} f_\alpha \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_\alpha} f_\alpha \nabla^{(n)} \cdot \mathsf{I}_\alpha^{(n)} \cdot \delta \mathbf{x} \, \mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_\alpha} f_\alpha \mathbf{n}_\alpha \cdot \delta \mathbf{x} \, \mathrm{d}\mathfrak{r} \quad \text{for } \alpha \in \mathfrak{J} \, . \qquad \text{(A.86)}$$

where $(n) = (3 - \dim \alpha)$ is the number of primes when $\dim \alpha$ is the dimensionality of α, and it is understood that when $\alpha \in \mathfrak{J}_\mathrm{C}$, the last integral over the boundary of the domain reverts to a sum over the points at the ends of the common curve. Additionally, $\mathsf{I}_\alpha^{(n)}$ consists of the unit tensor minus any elements that are orthogonal to the domain of interest such that with $\alpha \in \mathfrak{J}_\mathrm{P}$, $\mathsf{I}_\alpha = \mathsf{I}$; the other unit tensors have been previously defined.

Exercises

A.1. Confirm Eq. (A.72),

$$\sum_{i \in \mathfrak{J}_{\mathrm{Pt}_{\alpha\beta\gamma}}} \left(f_{\alpha\beta\gamma} \mathbf{n}_{\alpha\beta\gamma} \cdot \delta \mathbf{x} \right)\Big|_i = - \int\limits_{\Omega_\infty} f_{\alpha\beta\gamma} \left(\mathbf{n}_\alpha \cdot \nabla \Upsilon_\alpha \right) \left(\mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_{\alpha\beta} \right) \delta \mathbf{x} \cdot \nabla \Upsilon_{\alpha\beta\gamma} \, \mathrm{d}\mathfrak{r} \, .$$

A.2. Prove Eq. (A.75),

$$\mathbf{n}_\alpha \mathbf{n}_{\alpha\beta} : \nabla \nabla \Upsilon_\alpha = - \mathbf{n}_\alpha \cdot \nabla \mathbf{n}_{\alpha\beta} \cdot \nabla \Upsilon_\alpha \, .$$

A.3. Confirm Eq. (A.79),

$$\nabla \cdot \mathbf{n}_\alpha - \mathbf{n}_{\alpha\beta} \cdot \nabla \mathbf{n}_\alpha \cdot \mathbf{n}_{\alpha\beta} = - \mathbf{l}_{\alpha\beta\gamma} \cdot \nabla \mathbf{l}_{\alpha\beta\gamma} \cdot \mathbf{n}_\alpha \quad \text{for } \mathbf{x} \in \Omega_{\alpha\beta\gamma} \, .$$

A.4. If $\alpha \in \mathfrak{J}_\mathrm{Pt}$, provide the particular form of the variational equation based on Eq. (A.86) (Hint: Some of the integrals will be summations.).

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Appendix B
Derivations of Averaging Theorems

B.1 Overview

When an averaging operator is applied to a microscale conservation or balance equation for the purpose of transforming it to a larger scale, expressions involving averages of temporal and spatial derivatives arise. The averages of derivatives of microscale quantities are unknowns from a larger scale perspective and are not generally accessible. Simplification results if the averages of derivatives can be transformed into derivatives of averaged quantities. The purpose of this appendix is to derive a set of theorems that can be used to accomplish such transformations within the scope of this book. In the interest of completeness, these theorems are derived here, rather than just stated. The derivation approach makes use of indicator functions, as described in Sect. A.3, and of the ability of these functions to convert integrals over curves, surfaces, and volumes to integrals over all space [2]. Knowledge of the derivations of the theorems is not necessary for implementation of TCAT models, but the theorems themselves are an important tool in both changing conservation and balance equations from the microscale to the macroscale and in deriving additional conditions that are necessary for closure of macroscale models. The theorems to be employed here are a subset of the full range that can be developed and are those that are appropriate for integration over a macroscopic averaging volume that is invariant with time and with spatial position in a domain of interest. Sets of theorems beyond those to be considered here are needed to study domains that are megascopic in one or more spatial variables such that variability of a function in that spatial coordinate is not considered [1–3].

The process of averaging over a volume provides a change in perspective in viewing a model. For example, a property being differentiated may be associated with an entity that does not fill all of space. The averaging process results in measures of a property per volume. Thus, for example, an average of a fluid phase density gives the amount of fluid per volume, taking into account that the fluid phase may not be the only phase present. Similarly, the average of the mass per area of an interface is also normalized with respect to the averaging region such that the mass of

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material associated with a particular surface type per volume is obtained. The result of the averaging process is to obtain expressions for the derivatives of the average value of a function from the perspective of the larger scale. Thus, in averaging to the macroscale, we convert equations that express conservation within some subregion of the volume to a conservation equation for that property within the averaging region as a whole. The averaging process filters out variability of functions at a scale smaller than the macroscale, and this loss of explicit information provides one of the challenges to obtaining closure relations that implicitly account for smaller scale processes.

B.1.1 Naming Convention

We will follow a naming terminology for theorems consisting of a letter and a series of four numbers. The leading letter is D for a divergence theorem, G for a gradient theorem, and T for a transport theorem. The numbers are arranged in three groupings related to the dimensionality of the microscale, the macroscale, and the megascale. Two entries exist for the macroscale enclosed in parentheses, the first entry giving the number of macroscale dimensions for the domain and the second entry giving the number of macroscale dimensions evaluated at the boundary of the domain. Nine theorems will be needed for the TCAT models considered in this work—divergence, gradient, and transport theorem [3,(3,0),0], [2,(3,0),0], and [1,(3,0),0] families. The first of these families of theorems transforms an integral of a derivative of a microscale quantity in a three-dimensional volume domain into a derivative of an average over a three-dimensional macroscopic volume. The microscale integrals are associated with some subspace of the macroscale volume and thus need not occupy the full volume. The second family of theorems is needed to transform averages of surface derivatives of microscale quantities to derivatives of surface average values over three macroscale dimensions. The third family of theorems is needed to transform a derivative of a microscale quantity along a curve to a spatial derivative of the average value of that microscale quantity within an averaging volume containing the curve.

B.2 Coordinate Systems

In changing from a microscale to a macroscale perspective, we are also changing the coordinate system. Figure B.1 demonstrates that averaging volumes are located in space, and that integration is done over each averaging volume. Thus, the integration limits for the domain of integration are the same for each averaging volume if functions are provided in terms of coordinates relative to the centroid of the averaging volume and if the averaging volumes are independent of the locations of their centroids. For example, we can specify a vector function $\mathbf{f}(\mathbf{r},t)$, where $\mathbf{r}$ is

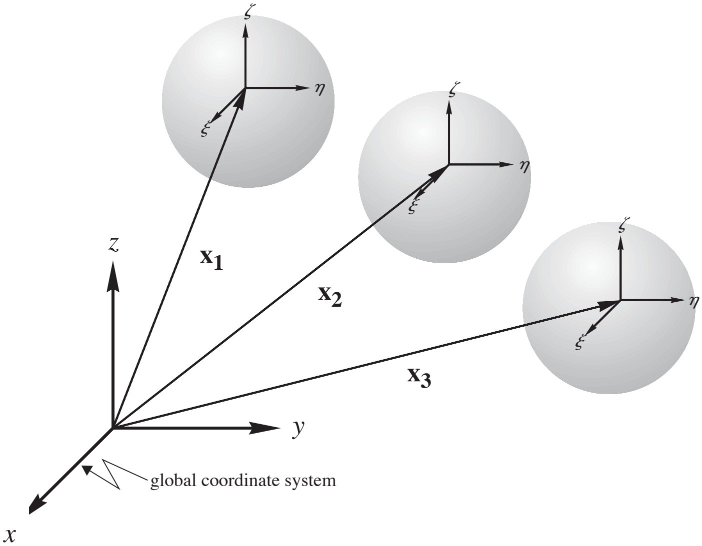

Fig. B.1 Global coordinate system, $\mathbf{x}$, used to locate averaging volumes in space provides centroid locations for averaging volumes and the local coordinate system, $\boldsymbol{\xi}$ (after [2])

the microscale coordinate system, as depending on the spatial coordinates $\mathbf{x}+\boldsymbol{\xi}$ as well as time so that we obtain $\mathbf{f}(\mathbf{x}+\boldsymbol{\xi},t)$. Since the function depends on the sum of the two coordinates, and not on each coordinate independently, a spatial derivative with respect to $\boldsymbol{\xi}$ coordinates while holding the $\mathbf{x}$ coordinates constant is equal to the spatial derivative with respect to $\mathbf{x}$ coordinates while holding the $\boldsymbol{\xi}$ coordinates constant, or

$$\nabla\cdot\mathbf{f} = \left(\nabla_{\boldsymbol{\xi}}\cdot\mathbf{f}\right)\Big|_{\mathbf{x}} = (\nabla_{\mathbf{x}}\cdot\mathbf{f})|_{\boldsymbol{\xi}} \ . \tag{B.1}$$

This observation has important implications when considering the integral of a divergence. Suppose we are going to perform averaging over a subregion, Ω, of a homogeneous region in space, as in Fig. B.1. Let us denote the closed boundary of Ω as Γ. Note that in this case, the geometry of the integration region is independent of the location of its centroid, and the coordinates of integration are the microscale coordinates. As a first example, suppose we are integrating $\left(\nabla_{\boldsymbol{\xi}}\cdot\mathbf{f}\right)\Big|_{\mathbf{x}}$ over the domain of the subregion, Ω. It is not possible to simply exchange the order of integration and differentiation because the variables of integration and differentiation are the same. However, we can apply the divergence theorem given by Eq. (2.10) to obtain

$$\int\limits_{\Omega} \left(\nabla_{\boldsymbol{\xi}}\cdot\mathbf{f}\right)\Big|_{\mathbf{x}} \mathrm{d}\mathfrak{r} = \int\limits_{\Gamma} \mathbf{n}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} \, . \tag{B.2}$$

We can now make use of the second equality in Eq. (B.1) to replace the integrand on the left side of Eq. (B.2). In this case, the coordinate of differentiation is different from the coordinate of integration. The divergence theorem may not be applied. However, because the integration domain is independent of the coordinates of differentiation, the order of integration and differentiation may be interchanged such that

$$\int_{\Omega} (\nabla_{\mathbf{x}} \cdot \mathbf{f})|_{\boldsymbol{\xi}} \, \mathrm{d}\mathfrak{r} = \nabla_{\mathbf{x}} \cdot \int_{\Omega} \mathbf{f} \, \mathrm{d}\mathfrak{r} \, . \tag{B.3}$$

Equation (B.2) is useful for converting an integral over the boundary of a domain to an integral of the divergence over the domain. This theorem has been employed in Chap. 2. Equation (B.3), on the other hand, provides a simple exchange of the order of differentiation and integration. Essentially this equation calculates the integral of the divergence on the left side and equates it to the divergence of the function integrated over a portion of space. Thus rather than associating microscale values with a point in space, an average, macroscale value over the region around each point is calculated and associated with that point. The divergence of this macroscale function at any point in space is then equal to the average over the region of the divergence of the microscale function. Similar reasoning can be employed to relate integrals of the divergence and the time derivative of a function.

If we were interested only in changing the scale of modeling a problem over a homogeneous region, our work in developing averaging theorems would be concluded. However, the fact that we will be changing the scale of problems described in porous media adds complications. Within any subregion sphere that we might identify, the portion of the space occupied by a particular phase and the distribution of interfaces and common curves within the sphere will be different. Therefore, we will make use of indicator functions to convert integration regions associated with an entity to a common averaging volume. Indicator functions have been used for this purpose in Appendix A.1, and their properties are described in Sect. A.3. In those sections, however, the macroscale and microscale coordinate designation was not needed; and discussion was in terms of a single spatial coordinate system. Nevertheless, the discussion translates well for the current objectives.

In the following derivations, the explicit distinction between the $\mathbf{x}$ and $\boldsymbol{\xi}$ coordinate systems will not be indicated. The context should provide a clear indication of the coordinate being employed for differentiation. The theorems here will be developed in a general context for volumes, surfaces, and curves. They will be listed as applied specifically to porous medium systems in Chap. 6.

B.3 Averaging Theorems for Volumes

The theorems in this family are applied to volumes and are useful, for example, for multiphase systems when one phase occupies part of space and other phases fill the rest of the space. Suppose we are interested in a portion of space with a domain denoted as $\Omega_V \subset \mathbb{R}^3$. We can thus make use of an indicator function Υ_V to denote locations within the global domain $\Omega_\infty \subset \mathbb{R}^3$ according to

$$\Upsilon_V(\mathbf{x}+\boldsymbol{\xi},t)=\begin{cases}1 & \text{for } \mathbf{x}+\boldsymbol{\xi}\in\Omega_V\\ 0 & \text{for } \mathbf{x}+\boldsymbol{\xi}\notin\Omega_V\end{cases} \; . \tag{B.4}$$

Because the indicator function undergoes an abrupt change in value at the boundary of Ω_V, it can be used to identify that location. The gradient of the indicator function is a directional delta function that converts the integral over space to the integral over the locations where the delta function acts such that

$$\int\limits_{\Omega_\infty} f\nabla\Upsilon_V\,\mathrm{d}\mathfrak{r}=-\int\limits_{\Gamma_V} f\mathbf{n}\,\mathrm{d}\mathfrak{r}\;, \tag{B.5}$$

where f is a scalar function, $\mathbf{n}$ is the unit vector outward normal from Ω_V, and Γ_V is the boundary of Ω_V.

Another identity of interest is for the total derivative of Υ_V, which can be expressed as

$$\frac{\mathrm{d}\Upsilon_V}{\mathrm{d}t}=\frac{\partial\Upsilon_V}{\partial t}+\frac{\mathrm{d}(\mathbf{x}+\boldsymbol{\xi})}{\mathrm{d}t}\cdot\nabla\Upsilon_V\;. \tag{B.6}$$

If the reference velocity, $\mathrm{d}(\mathbf{x}+\boldsymbol{\xi})/\mathrm{d}t$, is equivalent to the velocity of the boundary of Ω_V, denoted as $\mathbf{w}$, then the total derivative will be zero and we obtain

$$\frac{\partial\Upsilon_V}{\partial t}=-\mathbf{w}\cdot\nabla\Upsilon_V\;. \tag{B.7}$$

In the theorems to be derived here, we will be considering a global domain Ω_∞. The portion of the global domain that is of interest is denoted $\Omega_V\subset\Omega_\infty$. For example, Ω_V might be the portion of Ω_∞ occupied by a particular phase of interest. The averaging volume domain is denoted Ω, with boundary denoted Γ, and has a length scale much less than that of Ω_∞ but large enough that it contains a characteristic sample of the regions of interest in Ω_∞. The geometry and extent of Ω is not dependent on the location of its centroid within space. Within averaging volume Ω is a portion of subdomain Ω_V, denoted $\Omega_v=\Omega\cap\Omega_V$. The boundary of Ω_v is Γ_v, and it consists of two parts such that $\Gamma_v=\Gamma_{v\mathrm{i}}\cup\Gamma_{v\mathrm{e}}$. The portion of Γ_v that is within Ω is termed the internal boundary and is denoted $\Gamma_{v\mathrm{i}}\subset\Gamma_V$. The portion of Γ_v that coincides with the boundary of Ω is termed the external boundary and is defined as $\Gamma_{v\mathrm{e}}=\Gamma_v\cap\Gamma\not\subset\Gamma_V$. Therefore, if we consider an equation similar to Eq. (B.5) but use Ω as the spatial domain, we obtain

$$\int\limits_{\Omega} f\nabla\Upsilon_V\,\mathrm{d}\mathfrak{r}=-\int\limits_{\Gamma_{v\mathrm{i}}} f\mathbf{n}\,\mathrm{d}\mathfrak{r}\;. \tag{B.8}$$

The boundary $\Gamma_{v\mathrm{e}}$ does not enter into this equality because $\nabla\Upsilon_V$ is zero on $\Gamma_{v\mathrm{e}}$. The boundary $\Gamma_{v\mathrm{i}}$ is not a closed surface.

B.3.1 D[3,(3,0),0]

The integral of the divergence of a vector **f** over Ω_v can be converted to an integral over Ω by making use of the indicator function Υ_V with

$$\int_{\Omega_v} \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \int_{\Omega} \Upsilon_V \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,. \tag{B.9}$$

The generalized function has been introduced to change the region of integration to one that is independent of space. Application of the product rule to Eq. (B.9) yields

$$\int_{\Omega_v} \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \int_{\Omega} \nabla\cdot\left(\Upsilon_V\mathbf{f}\right)\,\mathrm{d}\mathfrak{r} - \int_{\Omega} \left(\nabla\Upsilon_V\right)\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,. \tag{B.10}$$

The divergence operator can be taken outside the first integral on the right side of Eq. (B.10) when the divergence operator is applied with respect to **x** coordinates; the second integral can be transformed using Eq. (B.8). Thus, Eq. (B.10) becomes

$$\int_{\Omega_v} \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int_{\Omega} \Upsilon_V\mathbf{f}\,\mathrm{d}\mathfrak{r} + \int_{\Gamma_{v\mathrm{i}}} \mathbf{n}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,. \tag{B.11}$$

Because the indicator function Υ_V here has the value of 1 in Ω_v and is zero elsewhere in Ω, it can be eliminated from the first integral on the right side when accompanied by a change in the domain of integration to Ω_v so that we obtain the desired theorem:

Theorem B.1 (D[3,(3,0),0])

$$\int_{\Omega_v} \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int_{\Omega_v} \mathbf{f}\,\mathrm{d}\mathfrak{r} + \int_{\Gamma_{v\mathrm{i}}} \mathbf{n}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,. \tag{B.12}$$

B.3.2 G[3,(3,0),0]

Similar manipulations as those used to derive the divergence theorem lead to the desired gradient theorem. A much simpler approach, however, is to select $\mathbf{f} = f\mathbf{b}$ where **b** is an arbitrary constant vector. Insertion of this specification of **f** into Eq. (B.12) directly provides the gradient averaging theorem:

Theorem B.2 (G[3,(3,0),0])

$$\int_{\Omega_v} \nabla f\,\mathrm{d}\mathfrak{r} = \nabla\int_{\Omega_v} f\,\mathrm{d}\mathfrak{r} + \int_{\Gamma_{v\mathrm{i}}} \mathbf{n}f\,\mathrm{d}\mathfrak{r}\,. \tag{B.13}$$

B.3.3 T[3,(3,0),0]

The integral over Ω_v of the partial derivative of a function f with respect to time can be converted to an integral over the entire averaging volume using the indicator function to obtain

$$\int_{\Omega_v} \frac{\partial f}{\partial t}\,\mathrm{d}\mathfrak{r} = \int_{\Omega} \Upsilon_V \frac{\partial f}{\partial t}\,\mathrm{d}\mathfrak{r}\,. \tag{B.14}$$

Application of the product rule to the right side of this equality yields

$$\int_{\Omega_v} \frac{\partial f}{\partial t}\,\mathrm{d}\mathfrak{r} = \int_{\Omega} \frac{\partial(\Upsilon_V f)}{\partial t}\,\mathrm{d}\mathfrak{r} - \int_{\Omega} \frac{\partial \Upsilon_V}{\partial t} f\,\mathrm{d}\mathfrak{r}\,. \tag{B.15}$$

The partial time derivative can be taken outside the first integral on the right side of Eq. (B.15) because Ω is independent of time, and the second integral can be transformed using Eq. (B.7). These changes give

$$\int_{\Omega_v} \frac{\partial f}{\partial t}\,\mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t}\int_{\Omega} \Upsilon_V f\,\mathrm{d}\mathfrak{r} + \int_{\Omega} \mathbf{w}\cdot\nabla\Upsilon_V f\,\mathrm{d}\mathfrak{r}\,. \tag{B.16}$$

The properties of Υ_V can be used to change the first integral on the right to an integral over Ω_v. The identity of Eq. (B.8) changes the last integral to an integral over the boundary such that we obtain the transport averaging theorem:

Theorem B.3 (T[3,(3,0),0])

$$\int_{\Omega_v} \frac{\partial f}{\partial t}\,\mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t}\int_{\Omega_v} f\,\mathrm{d}\mathfrak{r} - \int_{\Gamma_{\mathrm{vi}}} \mathbf{n}\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r}\,. \tag{B.17}$$

B.4 Averaging Theorems for Surfaces

A set of averaging theorems is also needed to transform integrals of derivatives on a surface to derivatives of integral quantities. The domain of a surface of interest within Ω_∞ is denoted as $\Omega_S \subset \mathbb{R}^2$. The theorems of interest apply to the case when portions and pieces of a surface occupying $\Omega_s \subset \Omega_S \subset \mathbb{R}^2$ are contained within the spatial averaging domain, $\Omega \subset \mathbb{R}^3$. It is desired to obtain expressions for spatial and temporal rates of change of the surface property throughout the system domain. We will consider the case when edges of the surface may exist within Ω_∞. For our purposes, a surface type of interest will be considered to be a boundary between two particular phases. Thus, when a physical surface of interest is identified that has an edge boundary within Ω_∞, it can be mathematically extended smoothly to the boundary of Ω_∞. This extended surface domain, including closed surfaces within Ω_∞, is denoted as $\Omega_{S\infty}$. A surface indicator function, Υ_S, may be employed on $\Omega_{S\infty}$

to identify Ω_S according to

$$\Upsilon_S(\mathbf{x}+\boldsymbol{\xi},t) = \begin{cases} 1 & \text{for } \mathbf{x}+\boldsymbol{\xi} \in \Omega_S \\ 0 & \text{for } \mathbf{x}+\boldsymbol{\xi} \notin \Omega_S \end{cases} . \tag{B.18}$$

The indicator function Υ_S undergoes an abrupt change in value at the edge of Ω_S. Thus, it may be used to identify that location. The surface gradient of this function is a directional delta function that is tangent to the surface and normal to the edge of the surface. Therefore

$$\int\limits_{\Omega_{S\infty}} f\nabla'\Upsilon_S \, \mathrm{d}\mathfrak{r} = -\int\limits_{\Gamma_S} f\mathbf{n}' \, \mathrm{d}\mathfrak{r} , \tag{B.19}$$

where Γ_S is the curve that bounds Ω_S within Ω_∞, $\mathbf{n}'$ is a unit vector oriented outward from Ω_S and tangent to the surface, and the surface gradient is

$$\nabla' = (\mathbf{I} - \mathbf{nn})\cdot\nabla , \tag{B.20}$$

with $\mathbf{n}$ being the unit vector normal to the surface. Note that, for example, if the boundary separates a bubble phase from a continuous phase, $\Omega_S = \Omega_{S\infty}$, and both sides of Eq. (B.19) will be zero.

The time derivative of Υ_S can be expressed as

$$\frac{\mathrm{d}\Upsilon_S}{\mathrm{d}t} = \frac{\partial'\Upsilon_S}{\partial t} + \frac{\mathrm{d}(\mathbf{x}+\boldsymbol{\xi})}{\mathrm{d}t}\cdot\nabla'\Upsilon_S , \tag{B.21}$$

where $\partial'/\partial t$ is the partial time derivative at a fixed surface coordinate with

$$\frac{\partial'}{\partial t} = \frac{\partial}{\partial t} + \mathbf{w}\cdot\mathbf{nn}\cdot\nabla . \tag{B.22}$$

When the reference velocity, $\mathrm{d}(\mathbf{x}+\boldsymbol{\xi})/\mathrm{d}t$ in Eq. (B.21), is equal to the velocity of the curve at the edge of Ω_S and is denoted as $\mathbf{w}$, the total time derivative will be zero and

$$\frac{\partial'\Upsilon_S}{\partial t} = -\mathbf{w}\cdot\nabla'\Upsilon_S . \tag{B.23}$$

We can also substitute Eqs. (B.20) and (B.22) into Eq. (B.23) to obtain

$$\frac{\partial\Upsilon_S}{\partial t} = -\mathbf{w}\cdot\nabla\Upsilon_S . \tag{B.24}$$

These considerations, along with the discussion of indicator functions for volumes, serve as a basis for deriving the averaging theorems for surfaces.

B.4.1 D[2,(3,0),0]

For this theorem, we seek to express the integral of a surface divergence of a function in terms of the spatial divergence of the function integrated over the surface. The region of integration is Ω_s, the portion of Ω_S within averaging volume Ω. The indicator function Υ_S can be used to change the domain of integration from Ω_s to Ω_{S_Ω} according to

$$\int\limits_{\Omega_s} \nabla'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_{S_\Omega}} \Upsilon_S \nabla'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,, \tag{B.25}$$

where Ω_{S_Ω} is the portion of the $\Omega_{S\infty}$ that is within the averaging volume, Ω. Equation (B.20) can be employed to change the surface divergence on the right side of this equation to a spatial divergence such that

$$\int\limits_{\Omega_s} \nabla'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_{S_\Omega}} \Upsilon_S \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_{S_\Omega}} \Upsilon_S \mathbf{n}\cdot\nabla\mathbf{f}\cdot\mathbf{n}\,\mathrm{d}\mathfrak{r}\,. \tag{B.26}$$

The domain of integration of the two integrals on the right side of Eq. (B.26) can be transformed into integration over Ω using the volume indicator function property given by Eq. (B.8), since Ω_{S_Ω} is the boundary of a volume within the averaging volume. The result is

$$\int\limits_{\Omega_s} \nabla'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = -\int\limits_{\Omega} \mathbf{n}\cdot\nabla\Upsilon_V \Upsilon_S \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} \Upsilon_S \mathbf{n}\cdot\nabla\mathbf{f}\cdot\nabla\Upsilon_V\,\mathrm{d}\mathfrak{r}\,, \tag{B.27}$$

where use has been made of the fact that

$$\mathbf{nn}\cdot\nabla\Upsilon_V = \nabla\Upsilon_V\,. \tag{B.28}$$

We now apply the product rule to the two integrals on the right side of Eq. (B.27) to obtain

$$\begin{aligned}\int\limits_{\Omega_s} \nabla'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = &-\int\limits_{\Omega} \nabla\cdot(\mathbf{fn}\cdot\nabla\Upsilon_V\Upsilon_S)\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} \mathbf{fn}{:}\nabla\nabla\Upsilon_V\Upsilon_S\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} \mathbf{n}\cdot\nabla\Upsilon_V\mathbf{f}\cdot\nabla\Upsilon_S\,\mathrm{d}\mathfrak{r}\\ &+\int\limits_{\Omega} \nabla\cdot(\mathbf{n}\Upsilon_S\mathbf{f}\cdot\nabla\Upsilon_V)\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} \nabla\cdot\mathbf{n}\Upsilon_S\mathbf{f}\cdot\nabla\Upsilon_V\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} \mathbf{fn}{:}\nabla\nabla\Upsilon_V\Upsilon_S\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{B.29}$$

The first three integrals on the right arise from the first term on the right of Eq. (B.27), and the last three integrals are from the second term on the right of Eq. (B.27). In obtaining this equation, use has been made of the fact that $\nabla\mathbf{n}\cdot\nabla\Upsilon_V$ and $\mathbf{n}\cdot\nabla\Upsilon_S$ are both zero. Because Ω is independent of space, the order of integration and differentiation can be exchanged in the first and fourth terms on the right. Additionally, the second and the sixth terms cancel so the net result is

$$\begin{aligned}\int\limits_{\Omega_s} \nabla' \cdot \mathbf{f} \, \mathrm{d}\mathfrak{r} = -\nabla \cdot \int\limits_{\Omega} \mathbf{f}\mathbf{n} \cdot \nabla \mathit{\Upsilon}_V \mathit{\Upsilon}_S \, \mathrm{d}\mathfrak{r} + \int\limits_{\Omega} \mathbf{n} \cdot \nabla \mathit{\Upsilon}_V \mathbf{f} \cdot \nabla \mathit{\Upsilon}_S \, \mathrm{d}\mathfrak{r} \\ + \nabla \cdot \int\limits_{\Omega} \mathbf{n} \mathit{\Upsilon}_S \mathbf{f} \cdot \nabla \mathit{\Upsilon}_V \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega} \nabla \cdot \mathbf{n} \mathit{\Upsilon}_S \mathbf{f} \cdot \nabla \mathit{\Upsilon}_V \, \mathrm{d}\mathfrak{r} \, . \qquad \text{(B.30)}\end{aligned}$$

We can eliminate $\nabla \mathit{\Upsilon}_V$ in favor of $-\mathbf{n}$ if we return the domains of integration of the integrals on the right to Ω_{S_Ω}. This gives us

$$\begin{aligned}\int\limits_{\Omega_s} \nabla' \cdot \mathbf{f} \, \mathrm{d}\mathfrak{r} = \nabla \cdot \int\limits_{\Omega_{S_\Omega}} \mathbf{f} \mathit{\Upsilon}_S \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_{S_\Omega}} \mathbf{f} \cdot \nabla \mathit{\Upsilon}_S \, \mathrm{d}\mathfrak{r} \\ - \nabla \cdot \int\limits_{\Omega_{S_\Omega}} \mathbf{n} \mathit{\Upsilon}_S \mathbf{f} \cdot \mathbf{n} \, \mathrm{d}\mathfrak{r} + \int\limits_{\Omega_{S_\Omega}} \nabla \cdot \mathbf{n} \mathit{\Upsilon}_S \mathbf{f} \cdot \mathbf{n} \, \mathrm{d}\mathfrak{r} \, . \qquad \text{(B.31)}\end{aligned}$$

The domains of integration of the first, third and fourth integrals on the right side can be changed to Ω_s because $\mathit{\Upsilon}_S = 1$ only on this portion of Ω_{S_Ω}. Additionally, the second integral becomes an integral over $\Gamma_{s\mathrm{i}}$, the boundary of Ω_s that occurs within Ω, because of the property of $\mathit{\Upsilon}_S$ indicated in Eq. (B.19). Similar to the case encountered for a volume, the boundary of the surface Ω_s, denoted $\Gamma_s = \Gamma_{s\mathrm{i}} \cup \Gamma_{s\mathrm{e}}$, can occur internal to Ω or external where the surface intersects the boundary of Ω. Thus, we obtain

$$\int\limits_{\Omega_s} \nabla' \cdot \mathbf{f} \, \mathrm{d}\mathfrak{r} = \nabla \cdot \int\limits_{\Omega_s} (\mathbf{f} - \mathbf{n}\mathbf{n} \cdot \mathbf{f}) \, \mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{s\mathrm{i}}} \mathbf{f} \cdot \mathbf{n}' \, \mathrm{d}\mathfrak{r} + \int\limits_{\Omega_s} (\nabla \cdot \mathbf{n}) \mathbf{f} \cdot \mathbf{n} \, \mathrm{d}\mathfrak{r} \, . \qquad \text{(B.32)}$$

Recall that the part of the unit tensor with entries such that it is in the surface is denoted $\mathbf{I}'$ where

$$\mathbf{I}' = \mathbf{I} - \mathbf{n}\mathbf{n} \qquad \text{(B.33)}$$

so that

$$\mathbf{I}' \cdot \mathbf{f} = \mathbf{f} - \mathbf{n}\mathbf{n} \cdot \mathbf{f} \, . \qquad \text{(B.34)}$$

Also, we can make use of the fact that $\nabla \cdot \mathbf{n} = \nabla' \cdot \mathbf{n}$ in conjunction with the surface divergence of Eq. (B.33) to show that

$$\nabla' \cdot \mathbf{I}' = -\left(\nabla' \cdot \mathbf{n}\right) \mathbf{n} \, . \qquad \text{(B.35)}$$

Insertion of Eqs. (B.34) and (B.35) into Eq. (B.32) provides the sought after theorem in the form:

Theorem B.4 (D[2,(3,0),0])

$$\int\limits_{\Omega_s} \nabla' \cdot \mathbf{f} \, \mathrm{d}\mathfrak{r} = \nabla \cdot \int\limits_{\Omega_s} \mathbf{I}' \cdot \mathbf{f} \, \mathrm{d}\mathfrak{r} - \int\limits_{\Omega_s} \nabla' \cdot \mathbf{I}' \cdot \mathbf{f} \, \mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{s\mathrm{i}}} \mathbf{n}' \cdot \mathbf{f} \, \mathrm{d}\mathfrak{r} \, . \qquad \text{(B.36)}$$

B.4.2 G[2,(3,0),0]

Similar manipulations as those used to derive the divergence theorem lead to the desired gradient theorem. Alternatively, one may follow a simpler approach by selecting $\mathbf{f} = f\mathbf{b}$ in Eq. (B.36), where $\mathbf{b}$ is an arbitrary constant vector, to obtain:

Theorem B.5 (G[2,(3,0),0])

$$\int\limits_{\Omega_s} \nabla' f \,\mathrm{d}\mathfrak{r} = \nabla\cdot \int\limits_{\Omega_s} \mathbf{I}' f \,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_s} \nabla'\cdot\mathbf{I}' f \,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma_{s\mathrm{i}}} \mathbf{n}' f \,\mathrm{d}\mathfrak{r} \,. \tag{B.37}$$

B.4.3 T[2,(3,0),0]

The integral over Ω_s within Ω of the partial time derivative restricted to that surface can be transformed using identity Eq. (B.22) so that

$$\int\limits_{\Omega_s} \frac{\partial' f}{\partial t} \,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_s} \frac{\partial f}{\partial t} \,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_s} \mathbf{w}\cdot\mathbf{n}\mathbf{n}\cdot\nabla f \,\mathrm{d}\mathfrak{r} \,. \tag{B.38}$$

Then the domains of integration on the right side can be transformed to Ω, analogously to the statement of Eq. (B.27) based on Eq. (B.26), so that

$$\int\limits_{\Omega_s} \frac{\partial' f}{\partial t} \,\mathrm{d}\mathfrak{r} = -\int\limits_{\Omega} \Upsilon_S \mathbf{n}\cdot\nabla\Upsilon_V \frac{\partial f}{\partial t} \,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} \Upsilon_S \mathbf{w}\cdot\mathbf{n}\nabla\Upsilon_V\cdot\nabla f \,\mathrm{d}\mathfrak{r} \,. \tag{B.39}$$

Apply the product rule to each of the integrals on the right side with respect to the differential operators acting on f to obtain

$$\begin{aligned} \int\limits_{\Omega_s} \frac{\partial' f}{\partial t} \,\mathrm{d}\mathfrak{r} = &-\int\limits_{\Omega} \frac{\partial}{\partial t} \left(\Upsilon_S \mathbf{n}\cdot\nabla\Upsilon_V f\right) \mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f \frac{\partial}{\partial t} \left(\Upsilon_S \mathbf{n}\cdot\nabla\Upsilon_V\right) \mathrm{d}\mathfrak{r} \\ &- \int\limits_{\Omega} \nabla\cdot\left(\nabla\Upsilon_V \Upsilon_S \mathbf{w}\cdot\mathbf{n} f\right) \mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f\nabla\cdot\left(\nabla\Upsilon_V \Upsilon_S \mathbf{w}\cdot\mathbf{n}\right) \mathrm{d}\mathfrak{r} \,. \end{aligned} \tag{B.40}$$

The differential operators may be moved outside of the first and third integrals on the right side, and the properties of the indicator functions can then be employed to change the domains from Ω to Ω_s. We observe that because $\nabla\Upsilon_V$ is a vector collinear with $\mathbf{n}$,

$$\mathbf{n}\nabla\Upsilon_V = \nabla\Upsilon_V \mathbf{n} \,. \tag{B.41}$$

This identity may be inserted into the last integral in Eq. (B.40). With these changes we obtain

$$\int\limits_{\Omega_s} \frac{\partial' f}{\partial t}\,\mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t}\int\limits_{\Omega_s} f\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f\frac{\partial}{\partial t}\left(\Upsilon_S \mathbf{n}\cdot\nabla\Upsilon_V\right)\mathrm{d}\mathfrak{r}$$

$$+\nabla\cdot\int\limits_{\Omega_s} \mathbf{n}\mathbf{n}\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f\nabla\cdot\left(\mathbf{n}\Upsilon_S \mathbf{w}\cdot\nabla\Upsilon_V\right)\mathrm{d}\mathfrak{r}\,. \tag{B.42}$$

At this point, we will concentrate on rearrangement of the second integrand on the right side of Eq. (B.42). Expand out the derivative in this term, dropping the part that is zero because $\partial\mathbf{n}/\partial t$ is orthogonal to $\nabla\Upsilon_V$, such that

$$\int\limits_{\Omega_s} \frac{\partial' f}{\partial t}\,\mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t}\int\limits_{\Omega_s} f\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f\frac{\partial \Upsilon_S}{\partial t}\mathbf{n}\cdot\nabla\Upsilon_V\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f\Upsilon_S\mathbf{n}\cdot\nabla\frac{\partial\Upsilon_V}{\partial t}\,\mathrm{d}\mathfrak{r}$$

$$+\nabla\cdot\int\limits_{\Omega_s} \mathbf{n}\mathbf{n}\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f\nabla\cdot\left(\mathbf{n}\Upsilon_S \mathbf{w}\cdot\nabla\Upsilon_V\right)\mathrm{d}\mathfrak{r}\,. \tag{B.43}$$

Eliminate the partial time derivatives of the indicator functions by substituting Eqs. (B.24) and (B.7) into the second and third integrands on the right side, respectively, which gives

$$\int\limits_{\Omega_s} \frac{\partial' f}{\partial t}\,\mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t}\int\limits_{\Omega_s} f\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} f\mathbf{w}\cdot\nabla\Upsilon_S\mathbf{n}\cdot\nabla\Upsilon_V\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} f\Upsilon_S\mathbf{n}\cdot\nabla\left(\mathbf{w}\cdot\nabla\Upsilon_V\right)\mathrm{d}\mathfrak{r}$$

$$+\nabla\cdot\int\limits_{\Omega_s} \mathbf{n}\mathbf{n}\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f\nabla\cdot\left(\mathbf{n}\Upsilon_S \mathbf{w}\cdot\nabla\Upsilon_V\right)\mathrm{d}\mathfrak{r}\,. \tag{B.44}$$

The second integral on the right side becomes an integral over the internal boundary of the surface. The third integral combines readily with the last one via the product rule so that the equation becomes

$$\int\limits_{\Omega_s} \frac{\partial' f}{\partial t}\,\mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t}\int\limits_{\Omega_s} f\,\mathrm{d}\mathfrak{r} - \int\limits_{\Gamma_{\mathrm{si}}} \mathbf{n}'\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r} + \nabla\cdot\int\limits_{\Omega_s} \mathbf{n}\mathbf{n}\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} f\mathbf{w}\cdot\nabla\Upsilon_V\nabla\cdot\mathbf{n}\Upsilon_S\,\mathrm{d}\mathfrak{r}\,. \tag{B.45}$$

Finally, the last integral in this expression reverts to an integral over Ω_s when the properties of the indicator functions are invoked. Thus, with rearrangement of the order of the integrals and use of Eqs. (B.33) and (B.35) the result obtained is:

Theorem B.6 (T[2,(3,0),0])

$$\int\limits_{\Omega_s} \frac{\partial' f}{\partial t}\,\mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t}\int\limits_{\Omega_s} f\,\mathrm{d}\mathfrak{r} + \nabla\cdot\int\limits_{\Omega_s}\left(\mathbf{l}-\mathbf{l}'\right)\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_s}\nabla'\cdot\mathbf{l}'\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r} - \int\limits_{\Gamma_{\mathrm{si}}} \mathbf{n}'\cdot\mathbf{w} f\,\mathrm{d}\mathfrak{r}\,. \tag{B.46}$$

B.5 Averaging Theorems for Curves

The approach to deriving the divergence and gradient theorems for a curve is similar to the approach used to derive the corresponding theorems for a surface. The complicating difference is that an additional step is needed to transform the integration over a curve to an integration over the averaging volume. We denote the domain of the curves of interest within the spatial domain Ω_∞ as Ω_C. The theorems of interest apply to the parts of this curve domain, $\Omega_c \subset \Omega_C$, within the averaging volume Ω. Note that the curves and pieces of the curve may have endpoints within Ω_∞ and also within Ω. When curves terminate within the domain, we will either close them conceptually by connecting them to the end of another curve or extend them to the boundary of Ω_∞. Either approach yields a closed curve. The full domain consisting of the curves of interest and their extensions is denoted Ω_{C_∞}. An indicator function, Υ_C, is used to identify $\Omega_C \subset \Omega_{C_\infty}$ according to

$$\Upsilon_C(\mathbf{x}+\boldsymbol{\xi},t) = \begin{cases} 1 & \text{for } \mathbf{x}+\boldsymbol{\xi} \in \Omega_C \\ 0 & \text{for } \mathbf{x}+\boldsymbol{\xi} \notin \Omega_C \end{cases} . \tag{B.47}$$

Because Υ_C undergoes an abrupt change in value at the boundary point of Ω_C, it can be used to convert an integral over a curve to a summation of values at those points with

$$\int\limits_{\Omega_{C\infty}} f\nabla''\Upsilon_C \,\mathrm{d}\mathfrak{r} = -\sum_{m\in\mathfrak{I}_{\Gamma_C}} f\mathbf{n}''\,|_{\Gamma_{C_m}} , \tag{B.48}$$

where Γ_C is the set of points that are the bounds of the curves in Ω_C, Γ_{C_m} is a single bounding point from the set of all end points, $\mathbf{n}''$ is a unit vector oriented outward from and tangent to the curve at its end points, and

$$\nabla'' = \mathbf{ll}\cdot\nabla , \tag{B.49}$$

where $\mathbf{l}$ is the unit vector tangent to the curve.

The time derivative of the indicator function satisfies conditions similar to those for the the surficial and volumetric indicator functions with

$$\frac{\partial''\Upsilon_C}{\partial t} = -\mathbf{w}\cdot\nabla''\Upsilon_C \tag{B.50}$$

and

$$\frac{\partial\Upsilon_C}{\partial t} = -\mathbf{w}\cdot\nabla\Upsilon_C , \tag{B.51}$$

where

$$\frac{\partial''}{\partial t} = \frac{\partial}{\partial t} + \mathbf{w}\cdot(\mathbf{I}-\mathbf{ll})\cdot\nabla . \tag{B.52}$$

B.5.1 D[1,(3,0),0]

The integral of the divergence of a vector function **f** over the curve contained in the averaging domain can be rewritten according to

$$\int\limits_{\Omega_c} \nabla''\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \int\limits_{\Omega_c} \nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_c} \mathbf{n}\cdot\nabla\mathbf{f}\cdot\mathbf{n}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_c} \mathbf{n}'\cdot\nabla\mathbf{f}\cdot\mathbf{n}'\,\mathrm{d}\mathfrak{r}\,. \tag{B.53}$$

The integrals over the curve within the averaging volume can be converted to integrals over the averaging volume by introducing the indicator functions so that

$$\begin{aligned}\int\limits_{\Omega_c} \nabla''\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = &\int\limits_{\Omega} \Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{n}\cdot\nabla\Upsilon_V\nabla\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} \Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{n}\cdot\nabla\mathbf{f}\cdot\nabla\Upsilon_V\,\mathrm{d}\mathfrak{r}\\ &- \int\limits_{\Omega} \Upsilon_C\mathbf{n}\cdot\nabla\Upsilon_V\mathbf{n}'\cdot\nabla\mathbf{f}\cdot\nabla\Upsilon_S\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{B.54}$$

In anticipation of being able to move the divergence operator outside of the integral, we apply the product rule to each of the three integrands on the right side, which gives

$$\begin{aligned}\int\limits_{\Omega_c} \nabla''\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = &\int\limits_{\Omega} \nabla\cdot\left(\mathbf{f}\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{n}\cdot\nabla\Upsilon_V\right)\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} \mathbf{f}\cdot\nabla\left(\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{n}\cdot\nabla\Upsilon_V\right)\,\mathrm{d}\mathfrak{r}\\ &- \int\limits_{\Omega} \nabla\cdot\left(\mathbf{n}\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{f}\cdot\nabla\Upsilon_V\right)\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} \nabla\cdot\left(\mathbf{n}\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\nabla\Upsilon_V\right)\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\\ &- \int\limits_{\Omega} \nabla\cdot\left(\mathbf{n}'\Upsilon_C\mathbf{n}\cdot\nabla\Upsilon_V\mathbf{f}\cdot\nabla\Upsilon_S\right)\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} \nabla\cdot\left(\mathbf{n}'\Upsilon_C\mathbf{n}\cdot\nabla\Upsilon_V\nabla\Upsilon_S\right)\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,.\end{aligned} \tag{B.55}$$

The order of differentiation and integration may be exchanged in the first, third, and fifth terms on the right. After this is done, the indicator functions in those integrands may be eliminated in returning the domain of integration to the curve within domain Ω. Then these terms can be combined. The result of these steps is

$$\begin{aligned}\int\limits_{\Omega_c} \nabla''\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = &\nabla\cdot\int\limits_{\Omega_c} \mathbf{ll}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} \mathbf{f}\cdot\nabla\left(\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{n}\cdot\nabla\Upsilon_V\right)\,\mathrm{d}\mathfrak{r}\\ &+ \int\limits_{\Omega} \nabla\cdot\left(\mathbf{n}\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\nabla\Upsilon_V\right)\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega} \nabla\cdot\left(\mathbf{n}'\Upsilon_C\mathbf{n}\cdot\nabla\Upsilon_V\nabla\Upsilon_S\right)\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,,\end{aligned} \tag{B.56}$$

where

$$\mathbf{f}'' = \left(\mathbf{I} - \mathbf{nn} - \mathbf{n}'\mathbf{n}'\right)\cdot\mathbf{f} = \mathbf{ll}\cdot\mathbf{f}\,. \tag{B.57}$$

The next step is to expand out the remaining integrals using the product rule. The expansions lead to three terms that survive for each integral (i.e., quantities such as $\nabla\mathbf{n}\cdot\nabla\Upsilon_V$ do not survive since this inner product is zero). The expanded form is

$$\begin{aligned}\int_{\Omega_c} \nabla''\cdot\mathbf{f}\,d\mathfrak{r} = \nabla\cdot\int_{\Omega_c}\mathbf{ll}\cdot\mathbf{f}\,d\mathfrak{r} &- \int_{\Omega} \mathbf{f}\cdot\nabla\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{n}\cdot\nabla\Upsilon_V\,d\mathfrak{r}\\ &- \int_{\Omega} \Upsilon_C\mathbf{n}'\mathbf{f}:\nabla\nabla\Upsilon_S\mathbf{n}\cdot\nabla\Upsilon_V\,d\mathfrak{r} - \int_{\Omega}\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{nf}:\nabla\nabla\Upsilon_V\,d\mathfrak{r}\\ &+ \int_{\Omega} \nabla\cdot\mathbf{n}\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\nabla\Upsilon_V\cdot\mathbf{f}\,d\mathfrak{r} + \int_{\Omega}\Upsilon_C\mathbf{nn}':\nabla\nabla\Upsilon_S\nabla\Upsilon_V\cdot\mathbf{f}\,d\mathfrak{r}\\ &+ \int_{\Omega}\Upsilon_C\mathbf{n}'\cdot\nabla\Upsilon_S\mathbf{nf}:\nabla\nabla\Upsilon_V\,d\mathfrak{r} + \int_{\Omega}\nabla\cdot\mathbf{n}'\Upsilon_C\mathbf{n}\cdot\nabla\Upsilon_V\nabla\Upsilon_S\cdot\mathbf{f}\,d\mathfrak{r}\\ &+ \int_{\Omega}\Upsilon_C\mathbf{nn}':\nabla\nabla\Upsilon_V\nabla\Upsilon_S\cdot\mathbf{f}\,d\mathfrak{r} + \int_{\Omega}\Upsilon_C\mathbf{n}'\mathbf{f}:\nabla\nabla\Upsilon_S\mathbf{n}\cdot\nabla\Upsilon_V\,d\mathfrak{r}\,. \end{aligned}\tag{B.58}$$

In this equation, the second integral on the right side can be converted to a summation of quantities at the ends of the common curve within Ω (i.e., the set of points at the ends of the curves comprising Ω_c that are located within Ω, which will be denoted as Γ_{ci}). The third and the tenth integrals on the right side cancel, as do the fourth and the seventh. The fifth and the eighth integrals of the right side revert back to integrals over Ω_c. With these changes, we have

$$\begin{aligned}\int_{\Omega_c} \nabla''\cdot\mathbf{f}\,d\mathfrak{r} = \nabla\cdot\int_{\Omega_c}\mathbf{ll}\cdot\mathbf{f}\,d\mathfrak{r} &+ \sum_{m\in\mathfrak{I}_{\Gamma_{\mathrm{ci}}}} \mathbf{n}''\cdot\mathbf{f}\,\big|_{\Gamma_{\mathrm{ci}m}}\\ &+ \int_{\Omega_c}(\nabla\cdot\mathbf{n})\,\mathbf{n}\cdot\mathbf{f}\,d\mathfrak{r} + \int_{\Omega}\Upsilon_C\mathbf{nn}':\nabla\nabla\Upsilon_S\nabla\Upsilon_V\cdot\mathbf{f}\,d\mathfrak{r}\\ &+ \int_{\Omega_c}\left(\nabla\cdot\mathbf{n}'\right)\mathbf{n}'\cdot\mathbf{f}\,d\mathfrak{r} + \int_{\Omega}\Upsilon_C\mathbf{nn}':\nabla\nabla\Upsilon_V\nabla\Upsilon_S\cdot\mathbf{f}\,d\mathfrak{r}\,. \end{aligned}\tag{B.59}$$

To manage the two integrals that still contain indicator functions, we make use of the identities that arise directly from the product rule,

$$\mathbf{nn}':\nabla\nabla\Upsilon_S = -\mathbf{n}'\cdot\nabla\mathbf{n}\cdot\nabla\Upsilon_S \tag{B.60}$$

and

$$\mathbf{nn}':\nabla\nabla\Upsilon_V = -\mathbf{n}\cdot\nabla\mathbf{n}'\cdot\nabla\Upsilon_V\,. \tag{B.61}$$

Substitution of these identities into Eq. (B.59) and simplification of the integrals by eliminating the indicator functions while changing the limits of integration yields

$$\int\limits_{\Omega_c} \nabla''\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega_c} \mathbf{ll}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \sum_{m\in\mathfrak{I}_{\Gamma_{\mathrm{ci}}}} \mathbf{n}''\cdot\mathbf{f}\,|_{\Gamma_{\mathrm{ci}m}} + \int\limits_{\Omega_c} (\nabla\cdot\mathbf{n})\,\mathbf{n}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}$$
$$-\int\limits_{\Omega_c} \mathbf{n}'\cdot\nabla\mathbf{n}\cdot\mathbf{n}'\mathbf{n}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Omega_c} \left(\nabla\cdot\mathbf{n}'\right)\mathbf{n}'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_c} \mathbf{n}\cdot\nabla\mathbf{n}'\cdot\mathbf{nn}'\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,. \tag{B.62}$$

We can make use of the additional identities,

$$\nabla\cdot\mathbf{n} - \mathbf{n}'\cdot\nabla\mathbf{n}\cdot\mathbf{n}' = \mathbf{l}\cdot\nabla\mathbf{n}\cdot\mathbf{l} = -\mathbf{l}\cdot\nabla\mathbf{l}\cdot\mathbf{n} \tag{B.63}$$

and

$$\nabla\cdot\mathbf{n}' - \mathbf{n}\cdot\nabla\mathbf{n}'\cdot\mathbf{n} = \mathbf{l}\cdot\nabla\mathbf{n}'\cdot\mathbf{l} = -\mathbf{l}\cdot\nabla\mathbf{l}\cdot\mathbf{n}'\,, \tag{B.64}$$

which can be inserted into Eq. (B.62) to obtain

$$\int\limits_{\Omega_c} \nabla''\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega_c} \mathbf{ll}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \sum_{m\in\mathfrak{I}_{\Gamma_{\mathrm{ci}}}} \mathbf{n}''\cdot\mathbf{f}\,|_{\Gamma_{\mathrm{ci}m}} - \int\limits_{\Omega_c} \mathbf{l}\cdot\nabla\mathbf{l}\cdot\left(\mathbf{nn}+\mathbf{n}'\mathbf{n}'\right)\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,. \tag{B.65}$$

Because $\mathbf{l}\cdot\nabla\mathbf{l}$ is orthogonal to $\mathbf{l}$, this equation simplifies to the desired theorem:

Theorem B.7 (D[1,(3,0),0])

$$\int\limits_{\Omega_c} \nabla''\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega_c} \mathbf{ll}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_c} \mathbf{l}\cdot\nabla''\mathbf{l}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \sum_{m\in\mathfrak{I}_{\Gamma_{\mathrm{ci}}}} \mathbf{n}''\cdot\mathbf{f}\,|_{\Gamma_{\mathrm{ci}m}}\,. \tag{B.66}$$

B.5.2 G[1,(3,0),0]

A calculation analogous to that employed to yield Eq. (B.66) will lead to the gradient form of this theorem. A recommended simpler alternative approach is to select $\mathbf{f} = f\mathbf{b}$ where $\mathbf{b}$ is an arbitrary constant vector. This selection, in concert with Eq. (B.66), yields the gradient theorem for a curve:

Theorem B.8 (G[1,(3,0),0])

$$\int\limits_{\Omega_c} \nabla'' f\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega_c} \mathbf{ll}f\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega_c} \mathbf{l}\cdot\nabla''\mathbf{l}f\,\mathrm{d}\mathfrak{r} + \sum_{m\in\mathfrak{I}_{\Gamma_{\mathrm{ci}}}} \mathbf{n}''f\,|_{\Gamma_{\mathrm{ci}m}}\,. \tag{B.67}$$

B.5.3 T[1,(3,0),0]

The derivation of the averaging theorem for a time derivative on a curve using generalized functions is a rather lengthy exercise that follows along the lines of the proof of Eq. (B.66). There is no direct procedure for obtaining this equation from an earlier equation as there is in obtaining the gradient theorems from the divergence theorems. However, a far less arduous path to obtaining the T[1,(3,0),0] theorem is to use induction built on knowledge of the theorems derived already in this appendix.

Based on Eqs. (B.17) and (B.46), we expect T[1,(3,0),0] to begin as follows

$$\int\limits_{\Omega_c} \frac{\partial'' f}{\partial t} \, \mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t} \int\limits_{\Omega_c} f \, \mathrm{d}\mathfrak{r} + \dots \,, \tag{B.68}$$

where ... indicates that additional terms are needed. Comparison of the boundary terms in Eqs. (B.12) and (B.17), and also for Eqs. (B.36) and (B.46), suggests that we examine the boundary term of Eq. (B.66) for the form of this term in the time theorem. This procedure suggests the time derivative theorem will be

$$\int\limits_{\Omega_c} \frac{\partial'' f}{\partial t} \, \mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t} \int\limits_{\Omega_c} f \, \mathrm{d}\mathfrak{r} + \dots - \sum_{m \in \mathfrak{I}_{\Gamma_{\mathrm{ci}}}} \mathbf{n}'' \cdot \mathbf{w} f \, |_{\Gamma_{\mathrm{ci}m}} \,. \tag{B.69}$$

The second term on the right side of T[2,(3,0),0], Eq. (B.46), is the divergence of an integral of the vector component of $\mathbf{w}$ that is normal to the surface, $\left(\mathbf{I} - \mathbf{I}'\right) \cdot \mathbf{w}$, multiplied by f. If this perspective is extended to the time integral over a curve, we expect that velocity within this term for the interface will be $(\mathbf{I} - \mathbf{ll}) \cdot \mathbf{w}$ because this velocity is normal to the curve. Insertion of this term into Eq. (B.69) yields

$$\int\limits_{\Omega_c} \frac{\partial'' f}{\partial t} \, \mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t} \int\limits_{\Omega_c} f \, \mathrm{d}\mathfrak{r} + \nabla \cdot \int\limits_{\Omega_c} (\mathbf{I} - \mathbf{ll}) \cdot \mathbf{w} f \, \mathrm{d}\mathfrak{r} + \dots - \sum_{m \in \mathfrak{I}_{\Gamma_{\mathrm{ci}}}} \mathbf{n}'' \cdot \mathbf{w} f \, |_{\Gamma_{\mathrm{ci}m}} \,. \tag{B.70}$$

Finally, the next to the last term on the right side of D[2,(3,0),0] and T[2,(3,0),0], Eqs. (B.36) and (B.46), are very similar with $\mathbf{f}$ in the former replaced by $-\mathbf{w}f$ in the latter. Making a similar adjustment to the corresponding term in D[1,(3,0),0], Eq. (B.66), and inserting it into Eq. (B.70) we obtain:

Theorem B.9 (T[1,(3,0),0])

$$\int\limits_{\Omega_c} \frac{\partial'' f}{\partial t} \, \mathrm{d}\mathfrak{r} = \frac{\partial}{\partial t} \int\limits_{\Omega_c} f \, \mathrm{d}\mathfrak{r} + \nabla \cdot \int\limits_{\Omega_c} (\mathbf{I} - \mathbf{ll}) \cdot \mathbf{w} f \, \mathrm{d}\mathfrak{r} + \int\limits_{\Omega_c} \mathbf{l} \cdot \nabla'' \mathbf{l} \cdot \mathbf{w} f \, \mathrm{d}\mathfrak{r} - \sum_{m \in \mathfrak{I}_{\Gamma_{\mathrm{ci}}}} \mathbf{n}'' \cdot \mathbf{w} f \, |_{\Gamma_{\mathrm{ci}m}} \,. \tag{B.71}$$

The correctness of this theorem can be confirmed by complete derivation that makes use of the indicator functions.

B.6 Averaging Theorems for Points

An averaging theorem for a collection of points within a volume will involve a summation over the points rather than an integral over any continuous domain. A divergence operator restricted to act on a point would have all three coordinates fixed and is denoted

$$\nabla''' = \left(\mathbf{I} - \mathbf{nn} - \mathbf{n}'\mathbf{n}' - \mathbf{n}''\mathbf{n}''\right) \cdot \nabla \,. \tag{B.72}$$

This operator is zero because $(\mathbf{I} - \mathbf{nn} - \mathbf{n}'\mathbf{n}' - \mathbf{n}''\mathbf{n}'') = 0$. The fact that the microscale spatial derivative operator for a point is zero is consistent with the notion that spatial derivatives of a function associated with a discrete point that is isolated from all other points in the domain cannot be calculated. For this reason, theorems that involve microscale spatial derivatives, which would be designated D[0,(3, 0),0] and G[0,(3,0),0], do not exist. On the other hand, the time derivative of the value of a function fixed to the point can be calculated. Thus, the theorem T[0,(3,0),0] does exist.

Let the domain consisting of a set of points that are each located within Ω_∞ be denoted as $\Omega_{PT} \subset \mathbb{R}^0$. Then the domain of points within the integration region, Ω, is denoted as Ω_{pt} where $\Omega_{pt} \subset \Omega_{PT}$. A point does not have a boundary; and the velocity of the point, $\mathbf{w}$, will be equal to the velocity of any mass associated with the point, $\mathbf{v}$.

B.6.1 T[0,(3,0),0]

This theorem may be written down directly based on the forms of the other T theorems. With summations replacing the integrals, we obtain

Theorem B.10 (T[0,(3,0),0])

$$\sum_{m\in\mathfrak{I}_{\Omega_{pt}}} \left.\frac{\partial''' f}{\partial t}\right|_m = \frac{\partial}{\partial t}\left(\sum_{m\in\mathfrak{I}_{\Omega_{pt}}} f|_m\right) + \nabla\cdot\left(\sum_{m\in\mathfrak{I}_{\Omega_{pt}}} (\mathbf{v}f)|_m\right) . \tag{B.73}$$

It is worth noting that although the divergence does not exist at the microscale, the divergence of the summation of values over a region associated with a macroscale point is a meaningful quantity, as in the last term of Eq. (B.73).

Exercises

B.1. Prove the identity mentioned after Eq. (B.29),

$$\nabla\mathbf{n}\cdot\nabla\varUpsilon_V = \mathbf{0}\,.$$

B.2. Prove Eq. (B.35),

$$\nabla'\cdot\mathsf{I}' = -\left(\nabla'\cdot\mathbf{n}\right)\mathbf{n}\,.$$

B.3. Prove Eqs. (B.60) and (B.61), restated respectively as

a. $$\mathbf{n}\mathbf{n}'{:}\nabla\nabla\varUpsilon_S = -\mathbf{n}'\cdot\nabla\mathbf{n}\cdot\nabla\varUpsilon_S\,.$$

b. $$\mathbf{n}\mathbf{n}'{:}\nabla\nabla\varUpsilon_V = -\mathbf{n}\cdot\nabla\mathbf{n}'\cdot\nabla\varUpsilon_V\,.$$

B.4. Prove Eqs. (B.63) and (B.64), restated respectively as

a. $$\nabla\cdot\mathbf{n} - \mathbf{n}'\cdot\nabla\mathbf{n}\cdot\mathbf{n}' = \mathbf{l}\cdot\nabla\mathbf{n}\cdot\mathbf{l} = -\mathbf{l}\cdot\nabla\mathbf{l}\cdot\mathbf{n}\,.$$

b. $$\nabla\cdot\mathbf{n}' - \mathbf{n}\cdot\nabla\mathbf{n}'\cdot\mathbf{n} = \mathbf{l}\cdot\nabla\mathbf{n}'\cdot\mathbf{l} = -\mathbf{l}\cdot\nabla\mathbf{l}\cdot\mathbf{n}'\,.$$

B.5. Derive theorem G[2,(3,0),0], Eq. (B.67), using indicator functions.

B.6. Derive theorem T[1,(3,0),0], Eq. (B.71), using indicator functions.

B.7. Show that the averaging theorems D[3-n,(3,0),0] for $n \in \{0,1,2\}$ can be stated in a single expression as

$$\int\limits_{\Omega} \nabla^{(n)}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} = \nabla\cdot\int\limits_{\Omega} \mathsf{I}^{(n)}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} - \int\limits_{\Omega} \nabla^{(n)}\cdot\mathsf{I}^{(n)}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r} + \int\limits_{\Gamma} \mathbf{n}^{(n)}\cdot\mathbf{f}\,\mathrm{d}\mathfrak{r}\,, \tag{B.74}$$

where (n) is the number of primes that appear in the superscript, and the integration domain is of dimensionality $3-n$.

B.8. Show that the averaging theorems T[3-n,(3,0),0] for $n \in \{0,1,2,3\}$ can be stated in a single expression as

$$\begin{aligned}\int\limits_{\Omega} \frac{\partial^{(n)} f}{\partial t}\,\mathrm{d}\mathfrak{r} = {} & \frac{\partial}{\partial t}\int\limits_{\Omega} f\,\mathrm{d}\mathfrak{r} + \nabla\cdot\int\limits_{\Omega}\left(\mathsf{I} - \mathsf{I}^{(n)}\right)\cdot\mathbf{w}f\,\mathrm{d}\mathfrak{r} \\ & + \int\limits_{\Omega} \nabla^{(n)}\cdot\mathsf{I}^{(n)}\cdot\mathbf{w}f\,\mathrm{d}\mathfrak{r} - \int\limits_{\Gamma} \mathbf{n}^{(n)}\cdot\mathbf{w}f\,\mathrm{d}\mathfrak{r}\,, \end{aligned} \tag{B.75}$$

where (n) is the number of primes that appear in the superscript, and the integration domain is of dimensionality $3-n$.

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Appendix C
Constrained Entropy Inequality Derivations

C.1 CEI for Single-fluid-phase Flow, Eq. (9.43)

Some of the mathematical manipulations required to produce the CEI given as Eq. (9.43) from Eq. (9.32) are discussed in Sect. 9.4.4. Furthermore, a tabulation of the antecedent terms that lead to the lines in Eq. (9.43) is provided in Table 9.1. Our experience has shown that although the manipulations are relatively straightforward, the form desired to be obtained is not obvious; obtaining a CEI therefore presents challenges. Because this is an introductory text, we provide in this section a detailed construction of the CEI for single-fluid-phase flow from the augmented entropy inequality of Eq. (9.32). The exposition is intended to fill in the gaps that are inherent in the presentation of Table 9.1. We follow the table organization with groupings of lines in Eq. (9.43) considered in turn and relevant manipulations presented to aid understanding of the steps needed to derive the final form of the CEI as a combination of conservation and thermodynamic equations. The particular equations are indicated in the right margin of Eq. (9.32) so that the terms contributed by those equations are easily identified. Some terms that originate in a particular conservation equation are distributed into various lines of the CEI.

Lines 1–4

Lines 1–4 of Eq. (9.43) collect some terms from the equations listed in Table 9.1 directly as they appear in Eq. (9.32). The quantities h^{α} and b^{α} for $\alpha \in \mathfrak{I}$ are moved unchanged from $\mathcal{E}_{*}^{\overline{\overline{\alpha}}}$ and $\mathcal{S}_{*}^{\overline{\overline{\alpha}}}$, respectively, to lines 1 and 3. Terms involving the material derivatives of $\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}}$ and material derivatives of $\mu_{\alpha} - \mu^{\overline{\alpha}}$ for $\alpha \in \mathfrak{I}$ from $\mathcal{T}_{*}^{\overline{\overline{\alpha}}}$ are found in lines 1–4. Material derivatives of $\psi^{\overline{\alpha}}$ with $\alpha \in \mathfrak{I}$ are obtained from $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$. These material derivatives are found in lines 2 and 4. The remaining terms in lines 1–4, involving material derivatives of $K_{E}^{\overline{\overline{\alpha}}}$ and ψ_{α}, are obtained by doing some manipulations of terms originating in the conservation and balance equations, which are detailed below.

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The material derivative terms involving $K_E^{\overline{\overline{\alpha}}}$ that appear in $\mathcal{E}_*^{\overline{\overline{\alpha}}}$ are treated differently for each entity. For the w phase, we apply identity Eq. (7.49) to obtain

$$\varepsilon^{\overline{\overline{w}}}\rho^w\frac{\mathrm{D}^{\overline{w}}K_E^{\overline{\overline{w}}}}{\mathrm{D}t} = \underbrace{\left\langle \rho_w\frac{\mathrm{D}^{\overline{s}}K_E^{\overline{\overline{w}}}}{\mathrm{D}t}\right\rangle_{\Omega_w,\Omega}}_{2} \underbrace{+\varepsilon^{\overline{\overline{w}}}\rho^w\nabla K_E^{\overline{\overline{w}}}}_{20}\cdot\underbrace{(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}})}_{21}, \tag{C.1}$$

where an under-braced number indicates the line in Eq. (9.43) in which the denoted term appears.

For the solid phase, there is no need to change the velocity for the material derivative of $K_E^{\overline{\overline{s}}}$ that arises in $\mathcal{E}_*^{\overline{\overline{s}}}$, so we have

$$\varepsilon^{\overline{\overline{s}}}\rho^s\frac{\mathrm{D}^{\overline{s}}K_E^{\overline{\overline{s}}}}{\mathrm{D}t} = \underbrace{\left\langle \rho_s\frac{\mathrm{D}^{\overline{s}}K_E^{\overline{\overline{s}}}}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}}_{2} . \tag{C.2}$$

For the material derivative of $K_E^{\overline{\overline{ws}}}$ that arises from equation $\mathcal{E}_*^{\overline{\overline{ws}}}$ we first introduce the averaging operator to obtain

$$\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\frac{\mathrm{D}^{\overline{ws}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t} = \left\langle \rho_{ws}\frac{\mathrm{D}^{\overline{ws}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega} . \tag{C.3}$$

Making use of Eq. (7.85), with both $i\alpha$ and α replaced by ws, we modify the material derivative on the right side of this equation and obtain

$$\begin{aligned}\varepsilon^{\overline{\overline{ws}}}\rho^w\frac{\mathrm{D}^{\overline{ws}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t} =& \left\langle \rho_{ws}\frac{\mathrm{D}^{\prime\overline{s}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega} + \left\langle \rho_{ws}(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}})\cdot\nabla K_E^{\overline{\overline{ws}}}\right\rangle_{\Omega_{ws},\Omega}\\ &- \left\langle \rho_{ws}(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})\cdot(\mathbf{l}-\mathbf{l}'_{ws})\cdot\nabla K_E^{\overline{\overline{ws}}}\right\rangle_{\Omega_{ws},\Omega} .\end{aligned} \tag{C.4}$$

The last term in this expression can be rewritten as two terms by replacing $\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}$ with $(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}})+(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}})$. We then make use of the fact that macroscale quantities can be moved outside the averaging operator to obtain

$$\begin{aligned}\varepsilon^{\overline{\overline{ws}}}\rho^w\frac{\mathrm{D}^{\overline{ws}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t} =& \underbrace{\left\langle \rho_{ws}\frac{\mathrm{D}^{\prime\overline{s}}K_E^{\overline{\overline{ws}}}}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega}}_{4} + \underbrace{\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\nabla K_E^{\overline{\overline{ws}}}}_{22}\cdot\underbrace{(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}})}_{26}\\ &- \underbrace{\left\langle \rho_{ws}(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}})\cdot(\mathbf{l}-\mathbf{l}'_{ws})\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla K_E^{\overline{\overline{ws}}}}_{33}\\ &- \underbrace{\left\langle \rho_{ws}(\mathbf{l}-\mathbf{l}'_{ws})\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla K_E^{\overline{\overline{ws}}}\cdot(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}})}_{26} .\end{aligned} \tag{C.5}$$

The remaining entries in lines 1–4 involve the material derivative of ψ_α. The antecedent terms are the partial time derivative and the gravitational term from $\mathcal{G}_*^{\overline{\overline{\alpha}}}$. This pairing is considered individually for each entity. For the w phase, we can add the terms and add and subtract $\mathbf{v}^{\overline{s}}$ in the gravity portion of the sum to obtain

$$\begin{aligned}&\left\langle \rho_w \frac{\partial \psi_w}{\partial t}\right\rangle_{\Omega_w,\Omega} - \varepsilon^{\overline{\overline{w}}}\rho^w \mathbf{g}^{\overline{w}}\cdot\mathbf{v}^{\overline{w}} \\ &\quad = \left\langle \rho_w \frac{\partial \psi_w}{\partial t}\right\rangle_{\Omega_w,\Omega} - \varepsilon^{\overline{\overline{w}}}\rho^w\mathbf{g}^{\overline{w}}\cdot\mathbf{v}^{\overline{s}} - \varepsilon^{\overline{\overline{w}}}\rho^w\mathbf{g}^{\overline{w}}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right) .\end{aligned} \tag{C.6}$$

Introduction of the averaging operator in the second term on the right then provides

$$\begin{aligned}\left\langle \rho_w \frac{\partial \psi_w}{\partial t}\right\rangle_{\Omega_w,\Omega} - \varepsilon^{\overline{\overline{w}}}\rho^w \mathbf{g}^{\overline{w}}\cdot\mathbf{v}^{\overline{w}} &= \left\langle \rho_w \frac{\partial \psi_w}{\partial t}\right\rangle_{\Omega_w,\Omega} \\ &- \left\langle \rho_w \mathbf{g}_w\cdot\mathbf{v}^{\overline{s}}\right\rangle_{\Omega_w,\Omega} - \varepsilon^{\overline{\overline{w}}}\rho^w\mathbf{g}^{\overline{w}}\cdot\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right) .\end{aligned} \tag{C.7}$$

Because $\mathbf{g}_\alpha + \nabla\psi_\alpha = \mathbf{0}$, the material derivative may be introduced by summing the first two terms on the right of the equal sign so that we obtain

$$\left\langle \rho_w \frac{\partial \psi_w}{\partial t}\right\rangle_{\Omega_w,\Omega} - \varepsilon^{\overline{\overline{w}}}\rho^w \mathbf{g}^{\overline{w}}\cdot\mathbf{v}^{\overline{w}} = \underbrace{\left\langle \rho_w \frac{\mathrm{D}^{\overline{s}}\psi_w}{\mathrm{D}t}\right\rangle_{\Omega_w,\Omega}}_{2} - \underbrace{\varepsilon^{\overline{\overline{w}}}\rho^w\mathbf{g}^{\overline{w}}}_{20}\cdot\underbrace{\left(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}}\right)}_{21} . \tag{C.8}$$

For the s phase, the manipulations are similar, but there is no need to generate a relative velocity term. We obtain

$$\left\langle \rho_s \frac{\partial \psi_s}{\partial t}\right\rangle_{\Omega_s,\Omega} - \varepsilon^{\overline{\overline{s}}}\rho^s \mathbf{g}^{\overline{s}}\cdot\mathbf{v}^{\overline{s}} = \left\langle \rho_s \frac{\partial \psi_s}{\partial t}\right\rangle_{\Omega_s,\Omega} - \left\langle \rho_s \mathbf{g}_s\cdot\mathbf{v}^{\overline{s}}\right\rangle_{\Omega_s,\Omega} = \underbrace{\left\langle \rho_s \frac{\mathrm{D}^{\overline{s}}\psi_s}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}}_{2} . \tag{C.9}$$

For the ws interface, the manipulations are more involved. The necessary terms can be extracted from $\mathcal{G}_*^{\overline{\overline{\alpha}}}$ for $\alpha = ws$, and introduction of $\mathbf{v}^{\overline{s}}$ gives

$$\begin{aligned}&\left\langle \rho_{ws}\left[\frac{\partial'\psi_{ws}}{\partial t} + \mathbf{v}_{ws}\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}\right]\right\rangle_{\Omega_{ws},\Omega} - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}} \\ &\quad = \left\langle \rho_{ws}\left[\frac{\partial'\psi_{ws}}{\partial t} + \mathbf{v}_{ws}\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}\right]\right\rangle_{\Omega_{ws},\Omega} - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}\cdot\mathbf{v}^{\overline{s}} \\ &\qquad - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right) .\end{aligned} \tag{C.10}$$

We express the second term on the right side in terms of the averaging operator over the interface to obtain

$$\begin{aligned}&\left\langle\rho_{ws}\left[\frac{\partial'\psi_{ws}}{\partial t}+\mathbf{v}_{ws}\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}\right]\right\rangle_{\Omega_{ws},\Omega}-\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}}\\&\quad=\left\langle\rho_{ws}\left[\frac{\partial'\psi_{ws}}{\partial t}+\mathbf{v}_{ws}\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}-\mathbf{g}_{ws}\cdot\mathbf{v}^{\overline{s}}\right]\right\rangle_{\Omega_{ws},\Omega}\\&\qquad-\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right).\end{aligned}\tag{C.11}$$

We will make use of the identity

$$\mathbf{g}_{ws}=-\nabla'\psi_{ws}+\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}\tag{C.12}$$

so that Eq. (C.11) becomes

$$\begin{aligned}&\left\langle\rho_{ws}\left[\frac{\partial'\psi_{ws}}{\partial t}+\mathbf{v}_{ws}\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}\right]\right\rangle_{\Omega_{ws},\Omega}-\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}}\\&\quad=\left\langle\rho_{ws}\left[\frac{\partial'\psi_{ws}}{\partial t}+\mathbf{v}^{\overline{s}}\cdot\nabla'\psi_{ws}+\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}\right]\right\rangle_{\Omega_{ws},\Omega}\\&\qquad-\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right).\end{aligned}\tag{C.13}$$

A material derivative on the surface as defined in Eq. (7.84) is

$$\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t}=\frac{\partial'}{\partial t}+\mathbf{v}^{\overline{s}}\cdot\nabla'.\tag{C.14}$$

Insertion of this definition into Eq. (C.13) gives

$$\begin{aligned}&\left\langle\rho_{ws}\left[\frac{\partial'\psi_{ws}}{\partial t}+\mathbf{v}_{ws}\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}\right]\right\rangle_{\Omega_{ws},\Omega}-\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}\cdot\mathbf{v}^{\overline{ws}}\\&\quad=\underbrace{\left\langle\rho_{ws}\frac{\mathrm{D}'^{\overline{s}}\psi_{ws}}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega}}_{4}+\underbrace{\left\langle\rho_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\cdot\mathbf{g}_{ws}\right\rangle_{\Omega_{ws},\Omega}}_{28}\\&\qquad-\underbrace{\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mathbf{g}^{\overline{ws}}}_{23}\cdot\underbrace{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}_{26}.\end{aligned}\tag{C.15}$$

Lines 5 and 6

Elements from $\mathcal{S}_*^{\overline{\overline{\alpha}}}$, $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, $\mathcal{G}_*^{\overline{\overline{\alpha}}}$, and $\mathcal{T}_*^{\overline{\overline{s}}}$ can be manipulated using the product rule to yield the entries given in Lines 5 and 6 of the CEI. These terms involve entropy and heat fluxes along with a solid-phase stress-deformation term. The required manipulations are application of the product rule and algebraic rearrangement.

The term $\nabla\cdot(\varepsilon^{\overline{\overline{\alpha}}}\varphi^{\overline{\alpha}})$ for $\alpha\in\mathfrak{I}$ is moved directly from $\mathcal{S}_*^{\overline{\overline{\alpha}}}$ to lines 5 and 6. The terms involving $\mathbf{q}^{\overline{\alpha}}$ from $\mathcal{E}_*^{\overline{\overline{\alpha}}}$ and $\mathbf{q}_{\mathbf{g}}$ from $\mathcal{G}_*^{\overline{\overline{\alpha}}}$ can be combined and rearranged together according to

$$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}}\right)=\underbrace{\nabla\cdot\left[\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}\left(\mathbf{q}^{\overline{\overline{\alpha}}}+\mathbf{q}_{\mathbf{g}}\right)\right]}_{5,6}\underbrace{-\varepsilon^{\overline{\overline{\alpha}}}(\mathbf{q}^{\overline{\overline{\alpha}}}+\mathbf{q}_{\mathbf{g}})\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)}_{9,10}\,. \tag{C.16}$$

Completion of line 6 makes use of a term originating in equation $\mathcal{T}_*^{\overline{\overline{s}}}$ associated with the solid phase. It is obtained by application of the product rule to the term on the left of the following equation,

$$\begin{aligned}
&-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla\cdot\left\langle\left(\mathsf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathsf{C}_s}{j_s}\mathsf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\\
&\quad=\underbrace{-\nabla\cdot\left[\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\mathsf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathsf{C}_s}{j_s}\mathsf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]}_{6}\\
&\quad\underbrace{+\left\langle\left(\mathsf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathsf{C}_s}{j_s}\mathsf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{s}}}}\right)}_{10}\,.
\end{aligned} \tag{C.17}$$

Lines 7 and 8

Lines 7 and 8 of Eq. (9.43) are products of fluxes and deformation rate tensor forces. As noted in Table 9.1, these terms arise from equations $\mathcal{S}_*^{\overline{\overline{\alpha}}}$, $\mathcal{M}_*^{\overline{\overline{\alpha}}}$, $\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$, $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, $\mathcal{T}_*^{\overline{\overline{s}}}$, and $\mathcal{T}_*^{\overline{\overline{ws}}}$. For the most part, the terms are formed as a collection of terms in the various equations that have the factor $\mathsf{d}^{\overline{\overline{\alpha}}}$.

There is one instance when the product rule must be employed in forming lines 7 and 8. The energy equation, $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, has a term involving the stress tensor that can be expanded to obtain,

$$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathsf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}\right)=\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathsf{t}^{\overline{\overline{\alpha}}}\right)\cdot\mathbf{v}^{\overline{\alpha}}+\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}\mathsf{t}^{\overline{\overline{\alpha}}}{:}\left(\nabla\mathbf{v}^{\overline{\alpha}}\right)^{\mathrm{T}}\,. \tag{C.18}$$

Because $\mathsf{t}^{\overline{\overline{\alpha}}}$ is symmetric, this can be written as

$$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathsf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}\right)=\underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathsf{t}^{\overline{\overline{\alpha}}}\right)\cdot\mathbf{v}^{\overline{\alpha}}}_{\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}}+\underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}\mathsf{t}^{\overline{\overline{\alpha}}}{:}\mathsf{d}^{\overline{\overline{\alpha}}}}_{7,8}\quad\text{for }\alpha\in\mathfrak{I}\,, \tag{C.19}$$

where the first term on the right cancels with a like term originating from the momentum equation while the second term appears as part of lines 7 and 8 of the CEI.

The next task is to look through Eq. (9.32) and collect all the remaining terms that multiply $\mathsf{d}^{\overline{\overline{\alpha}}}$ on an entity-by-entity basis. Some of the terms cancel each other; but for the w phase, the terms that survive form the left side of the following equation,

$$-\frac{1}{\theta^{\overline{\overline{w}}}}\left(E^{\overline{\overline{w}}}-\eta^{\overline{\overline{w}}}\theta^{\overline{\overline{w}}}-\varepsilon^{\overline{\overline{w}}}\rho^{w}\mu^{\overline{w}}\right)\mathsf{I}{:}\mathbf{d}^{\overline{\overline{w}}}=\underbrace{\frac{1}{\theta^{\overline{\overline{w}}}}\varepsilon^{\overline{\overline{w}}}p^{w}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{w}}}}_{7}\,, \tag{C.20}$$

where use has been made of the Euler equation for the *w* phase comprised of a single species, Eq. (7.13) with $\alpha = w$,

$$E^{\overline{\overline{w}}}=\eta^{\overline{\overline{w}}}\theta^{\overline{\overline{w}}}-\varepsilon^{\overline{\overline{w}}}p^{w}+\varepsilon^{\overline{\overline{w}}}\rho^{w}\mu^{\overline{w}}\,. \tag{C.21}$$

For the solid phase, the multipliers of $\mathbf{d}^{\overline{\overline{s}}}$ in Eq. (9.32) are collected to obtain the expression on the left side of the following equation,

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left[\left(E^{\overline{\overline{s}}}-\eta^{\overline{\overline{s}}}\theta^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\frac{\mathbf{C}^{s}}{j^{s}}-\varepsilon^{\overline{\overline{s}}}\rho^{s}\mu^{\overline{s}}\right)\mathsf{I}+\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}\right]{:}\mathbf{d}^{\overline{\overline{s}}}=-\underbrace{\frac{1}{\theta^{\overline{\overline{s}}}}\varepsilon^{\overline{\overline{s}}}\mathbf{t}^{s}{:}\mathbf{d}^{\overline{\overline{s}}}}_{7}\,. \tag{C.22}$$

According to the Euler equation for the solid, given as as the fourth equation in Table 7.1, the quantity on the left side in parenthesis is zero, resulting in the simplification on the right side.

For the *ws* entity, the terms that multiply $\mathbf{d}^{\overline{\overline{ws}}}$ in Eq. (9.32) are collected on the left side of the following equation,

$$\begin{aligned}&-\frac{1}{\theta^{\overline{\overline{ws}}}}\left[\left(E^{\overline{\overline{ws}}}-\eta^{\overline{\overline{ws}}}\theta^{\overline{\overline{ws}}}-\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\mu^{\overline{ws}}\right)\mathsf{I}-\left\langle(\mathsf{I}-\mathsf{I}'_{ws})\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}\right]{:}\mathbf{d}^{\overline{\overline{ws}}}\\&=-\underbrace{\frac{1}{\theta^{\overline{\overline{ws}}}}\left[\varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\mathsf{I}-\left\langle(\mathsf{I}-\mathsf{I}'_{ws})\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}\right]{:}\mathbf{d}^{\overline{\overline{ws}}}}_{8}\,.\end{aligned} \tag{C.23}$$

The simplification obtained as the right side of the equation makes use of the macroscale Euler equation for an interface, the sixth equation in Table 7.1 with α replaced by *ws* and with only one chemical species.

Lines 9 and 10

These lines have already been completed as collateral terms from the preceding derivations. In particular the terms in these equations were obtained from the preceding equations as follows,

Line 9: Eq. (C.16); and
Line 10: Eqs. (C.16) and (C.17).

Line 11

These terms arise from $\mathcal{M}_*^{\overline{\overline{w}}}$ and $\mathcal{M}_*^{\overline{\overline{ws}}}$. The terms extracted are on the left of the following equation, and they are rearranged on the right side such that

$$-\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{w}}+\psi^{\overline{w}}+K_E^{\overline{\overline{w}}}\right)\overset{ws\to w}{M}-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{ws}}+\psi^{\overline{ws}}+K_E^{\overline{\overline{ws}}}\right)\overset{w\to ws}{M}$$

$$=\underbrace{\overset{w\to ws}{M}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{w}}+K_E^{\overline{\overline{w}}}+\psi^{\overline{w}}\right)-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\right]}_{11}, \qquad \text{(C.24)}$$

where use has been made of the fact that $\overset{w\to ws}{M}=-\overset{ws\to w}{M}$.

Line 12

This line is similar to line 11 with the exception being that the s phase is considered rather than the w phase. The terms in these lines arise from $\mathcal{M}_*^{\overline{\overline{s}}}$ and $\mathcal{M}_*^{\overline{\overline{ws}}}$. The terms collected are on the left of the following equation, and they are rearranged on the right side such that

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{s}}+\psi^{\overline{s}}+K_E^{\overline{\overline{s}}}\right)\overset{ws\to s}{M}-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{ws}}+\psi^{\overline{ws}}+K_E^{\overline{\overline{ws}}}\right)\overset{s\to ws}{M}$$

$$=\underbrace{\overset{s\to ws}{M}\left[\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{s}}+K_E^{\overline{\overline{s}}}+\psi^{\overline{s}}\right)-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{ws}}+K_E^{\overline{\overline{ws}}}+\psi^{\overline{ws}}\right)\right]}_{12}. \qquad \text{(C.25)}$$

Additionally, the following identity is used to add and subtract terms in Eq. (9.43),

$$\underbrace{\overset{s\to ws}{M}\frac{1}{\theta^{\overline{\overline{s}}}}\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^s}{3\rho^s j^s}}_{12}\underbrace{-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^s}{3\rho^s j^s}\rho_s(\mathbf{v}_s-\mathbf{v}_{ws})\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}}_{13}=0. \qquad \text{(C.26)}$$

Line 13

One term has already been provided to this line from Eq. (C.26). A second term comes from $\mathcal{T}_*^{\overline{\overline{s}}}$ with

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot(\mathbf{v}_{ws}-\mathbf{v}_s)\,\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Omega_{ws},\Omega}=\underbrace{\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{\rho_s j_s}\rho_s(\mathbf{v}_s-\mathbf{v}_{ws})\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}}_{13}. \qquad \text{(C.27)}$$

The other term in line 13 also originates in $\mathcal{T}_*^{\overline{\overline{s}}}$ but is rearranged by noting that

$$\begin{aligned}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega} &= -\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega}\\ &\quad -\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathsf{I}'_{ws}\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega}\,. \qquad \text{(C.28)}\end{aligned}$$

In this expression, use has been made of the identity

$$\mathsf{I}=\mathsf{I}'_{ws}+\mathbf{n}_s\mathbf{n}_s\,, \qquad \text{(C.29)}$$

where I'_{ws} was first defined in the statement of Theorem 2.3. The first term on the right side in Eq. (C.28) can be modified further by adding and subtracting $\mathbf{v}_{ws}$ and then multiplying and dividing by ρ_s to obtain

$$\begin{aligned}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega} &= -\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \frac{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s}{\rho_s}\rho_s(\mathbf{v}_s-\mathbf{v}_{ws})\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}\\ &\quad -\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathsf{I}'_{ws}\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega}\,. \qquad \text{(C.30)}\end{aligned}$$

The second term on the right is modified further by addition and subtraction of $1/\theta^{\overline{\overline{ws}}}$ with $1/\theta^{\overline{\overline{s}}}$ so that we obtain

$$\begin{aligned}-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega} &= \underbrace{-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \frac{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s}{\rho_s}\rho_s(\mathbf{v}_s-\mathbf{v}_{ws})\cdot\mathbf{n}_s\right\rangle_{\Omega_{ws},\Omega}}_{13}\\ &\quad -\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \underbrace{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s}_{27}\cdot\underbrace{(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})}_{28}\right\rangle_{\Omega_{ws},\Omega} \underbrace{-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathsf{I}'_{ws}\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega}}_{29}\\ &\quad \underbrace{-\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_{ws},\Omega}}_{19}\,. \qquad \text{(C.31)}\end{aligned}$$

Lines 14–16, 17–19

The terms in this pair of three-line segments of the equation are descriptive of energy exchanges between the *w* and *ws* entities and between the *s* and *ws* entities, respectively. Thus far, only a term from Eq. (C.31) has gone into these lines; it appears in line 19. An additional term involving p_w is obtained from $\mathcal{T}_*^{\overline{\overline{w}}}$ with the following manipulation,

$$\frac{1}{\theta^{\overline{\overline{w}}}}\left\langle \mathbf{n}_w\cdot(\mathbf{v}_{ws}-\mathbf{v}^{\bar{s}})p_w\right\rangle_{\Omega_{ws},\Omega} = \underbrace{\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\left\langle \mathbf{n}_w\cdot(\mathbf{v}_{ws}-\mathbf{v}^{\bar{s}})p_w\right\rangle_{\Omega_{ws},\Omega}}_{16}$$

$$+\underbrace{\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \mathbf{n}_w\cdot(\mathbf{v}_{ws}-\mathbf{v}^{\bar{s}})p_w\right\rangle_{\Omega_{ws},\Omega}}_{27,28}\,. \tag{C.32}$$

The antecedent terms for the rest of the lines are all the terms in Eq. (9.32) that have not already been worked with in obtaining lines 11 and 12 that contain inter-entity exchanges. For convenience, we will denote this collection of exchange terms as X. These terms originate in $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, $\mathcal{P}_*^{\overline{\overline{\alpha}}}$, $\mathcal{M}_*^{\overline{\overline{\alpha}}}$, and $\mathcal{G}_*^{\overline{\overline{\alpha}}}$ for $\alpha\in\mathfrak{J}$. The terms of interest are

$$\begin{aligned}
X = {} & \sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left[\overline{E}^{\overline{\overline{\alpha,\kappa}}}+\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}}{2}+K_E^{\overline{\overline{\alpha,\kappa}}}\right] \\
& +\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{\kappa\to\alpha}{Q}\right] \\
& -\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\alpha}}-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathbf{v}^{\overline{\alpha}}\cdot\overset{\kappa\to\alpha}{\mathbf{T}} \\
& +\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\right)\overset{\kappa\to\alpha}{M} \\
& +\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\psi^{\overline{\overline{\alpha,\kappa}}}+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{\kappa\to\alpha}{G}\,.
\end{aligned} \tag{C.33}$$

Terms are listed in the preceding equation in the order in which they arise in Eq. (9.32). The bulk of the manipulations to be done involves rearranging the equation so that all velocities are relative to $\mathbf{v}^{\bar{s}}$. We proceed by first reordering the terms so that the ones involving products of velocity with mass exchange are the last terms in the listing,

$$\begin{aligned}
X = {} & \sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\overset{\kappa\to\alpha}{Q}+\overset{\kappa\to\alpha}{G}\right)+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}}+K_E^{\overline{\overline{\alpha,\kappa}}}+\psi^{\overline{\overline{\alpha,\kappa}}}\right) \\
& +\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\alpha}} \\
& +\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}}{2}-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}\cdot\mathbf{v}^{\overline{\alpha}} \\
& +\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\,.
\end{aligned} \tag{C.34}$$

The last three group of summations are readily combined so that we have

$$\begin{aligned}X = &\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\overset{\kappa\to\alpha}{Q} + \overset{\kappa\to\alpha}{G}\right) + \sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}} + K_E^{\overline{\overline{\alpha,\kappa}}} + \psi^{\overline{\overline{\alpha,\kappa}}}\right)\\ &+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\alpha}}\\ &+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left[\frac{\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{\alpha}}\right)}{2}\right]\,. \end{aligned}\qquad\text{(C.35)}$$

With the equation in this form, we can subtract $\mathbf{v}^{\overline{s}}$ from each velocity, since this reference velocity will cancel out of the equation. We thus have

$$\begin{aligned}X = &\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\overset{\kappa\to\alpha}{Q} + \overset{\kappa\to\alpha}{G}\right) + \sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}} + K_E^{\overline{\overline{\alpha,\kappa}}} + \psi^{\overline{\overline{\alpha,\kappa}}}\right)\\ &+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}}\right) - \sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)\\ &+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\frac{1}{2}\left\{\left[\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}}\right) - \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)\right]\right.\\ &\qquad\left.\cdot\left[\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}}\right) - \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)\right]\right\}\,. \end{aligned}\qquad\text{(C.36)}$$

The group of terms in the last summation now can be expanded, making sure to retain velocities relative to $\mathbf{v}^{\overline{s}}$. After this expansion, the terms are grouped to obtain

$$\begin{aligned}X = &\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\overset{\kappa\to\alpha}{Q} + \overset{\kappa\to\alpha}{G}\right) + \sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}} + K_E^{\overline{\overline{\alpha,\kappa}}} + \psi^{\overline{\overline{\alpha,\kappa}}}\right)\\ &+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\overset{\kappa\to\alpha}{\mathbf{T}} + \overset{\kappa\to\alpha}{M}\left(\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}}}{2}\right)\right]\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}}\right)\\ &-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\overset{\kappa\to\alpha}{\mathbf{T}} - \overset{\kappa\to\alpha}{M}\left[\frac{\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}}{2} - \left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}}\right)\right]\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)\,. \end{aligned}\qquad\text{(C.37)}$$

The derivation is completed by expanding out the summations over α and κ. Also, all the exchange terms are written so that the transfer is from a phase to the interface (i.e., the negative of a transfer from the interface to a phase). Expansion of the summations then yields

$$X = -\left\{\underbrace{\overset{w\to ws}{Q} + \overset{w\to ws}{G} + \left(\overline{E}_w^{\overline{\overline{ws}}} + K_{Ew}^{\overline{\overline{ws}}} + \psi_w^{\overline{\overline{ws}}}\right)\overset{w\to ws}{M}}_{14}\right.$$

$$\underbrace{+\left[\overset{w\to ws}{\mathbf{T}}+\left(\frac{\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\bar{s}}}{2}\right)\overset{w\to ws}{M}\right]\cdot\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\bar{s}}\right)}_{15}\Bigg\}\underbrace{\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)}_{16}$$

$$-\Bigg\{\underbrace{\overset{s\to ws}{Q}+\overset{s\to ws}{G}+\left(\overline{E}_s^{\overline{ws}}+K_{Es}^{\overline{\overline{ws}}}+\psi_s^{\overline{ws}}\right)\overset{s\to ws}{M}}_{17}$$

$$\underbrace{+\left[\overset{s\to ws}{\mathbf{T}}+\left(\frac{\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\bar{s}}}{2}\right)\overset{s\to ws}{M}\right]\cdot\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\bar{s}}\right)}_{18}\Bigg\}\underbrace{\left(\frac{1}{\theta^{\bar{\bar{s}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)}_{19}$$

$$\underbrace{+\frac{1}{\theta^{\overline{\overline{w}}}}\left\{\overset{w\to ws}{\mathbf{T}}-\overset{w\to ws}{M}\left[\frac{\mathbf{v}^{\bar{w}}-\mathbf{v}^{\bar{s}}}{2}-\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\bar{s}}\right)\right]\right\}\cdot\left(\mathbf{v}^{\bar{w}}-\mathbf{v}^{\bar{s}}\right)}_{21}$$

$$\underbrace{-\frac{1}{\theta^{\overline{\overline{ws}}}}\Bigg\{\overset{w\to ws}{\mathbf{T}}-\overset{w\to ws}{M}\left[\frac{\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\bar{s}}}{2}-\left(\mathbf{v}_w^{\overline{ws}}-\mathbf{v}^{\bar{s}}\right)\right]}_{23}$$

$$\underbrace{+\overset{s\to ws}{\mathbf{T}}-\overset{s\to ws}{M}\left[\frac{\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\bar{s}}}{2}-\left(\mathbf{v}_s^{\overline{ws}}-\mathbf{v}^{\bar{s}}\right)\right]}_{24}\Bigg\}\cdot\underbrace{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\bar{s}}\right)}_{26}\,. \tag{C.38}$$

As suggested in Table 9.1, the exchange terms that arise from the momentum equation, $\mathcal{P}_*^{\overline{\overline{\alpha}}}$, do not contribute to lines 14–19. They become parts of the terms that multiply velocity differences, $\mathbf{v}^{\bar{w}}-\mathbf{v}^{\bar{s}}$ and $\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\bar{s}}$.

Lines 20 and 21

Some of these terms have already been obtained from Eqs. (C.1), (C.8), and (C.38). The remaining terms transfer directly from $\mathcal{T}_*^{\overline{\overline{w}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{w}}}$. They are the parts of these equations that multiply $\mathbf{v}^{\bar{w}}-\mathbf{v}^{\bar{s}}$.

Lines 22–26

Many of the terms needed to form lines 22–26 have already been obtained from Eqs. (C.1), (C.15), and (C.38). A few terms transfer directly from the parts of $\mathcal{T}_*^{\overline{\overline{ws}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$ that multiply $\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\bar{s}}$. Additional terms that appear in these lines are obtained from rearrangement of contributions from $\mathcal{T}_*^{\overline{\overline{ws}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$. The terms extracted appear on the left side of the following equation, and are rearranged on the right side with

$$\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle\eta_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\bar{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\theta^{\overline{\overline{ws}}}$$

$$
\begin{aligned}
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \rho_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\mu^{\overline{ws}}\\
&+\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \rho_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\psi^{\overline{iws}}\\
=&\underbrace{\frac{1}{\theta^{\overline{\overline{ws}}}}}_{22}\underbrace{\left[\left\langle \eta_{ws}\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\theta^{\overline{\overline{ws}}}\right]}_{25}\cdot\underbrace{\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}_{26}\\
&\underbrace{+\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \eta_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\theta^{\overline{\overline{ws}}}}_{31}\\
&+\underbrace{\frac{1}{\theta^{\overline{\overline{ws}}}}}_{22}\underbrace{\left[\left\langle \rho_{ws}\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\left(\mu^{\overline{ws}}+\psi^{\overline{ws}}\right)\right]\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}_{26}\\
&\underbrace{+\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \rho_{ws}\left(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\left(\mu^{\overline{ws}}+\psi^{\overline{ws}}\right)}_{33}\ . \qquad \text{(C.39)}
\end{aligned}
$$

Line 27 and 28

Contributions to these lines have been made as byproducts of other manipulations according to Eqs. (C.15), (C.31), and (C.32). Additionally, the term involving γ_{ws} is acquired directly from $\mathcal{T}_{*}^{\overline{\overline{ws}}}$.

Lines 29–34

These lines have been produced, for the most part, from the manipulations to obtain terms for the preceding lines. Other terms are directly transferred without rearrangement from an antecedent equation. The origins of these six lines are,

Line 29: Eq. (C.31);
Line 30: This is obtained directly from $\mathcal{T}_{*}^{\overline{\overline{s}}}$;
Line 31: Eq. (C.39);
Line 32: This is obtained directly from $\mathcal{T}_{*}^{\overline{\overline{ws}}}$;
Line 33: Eqs. (C.5) and (C.39);
Line 34: This is obtained directly from $\mathcal{S}_{*}^{\overline{\overline{\alpha}}}$ for $\alpha \in \mathfrak{I}$.

C.2 CEI for Single-fluid-phase Transport, Eq. (10.14)

The manipulations required to produce the CEI in Eq. (10.14) from Eq. (10.13), as summarized in Table 10.2, are detailed in this section. The manipulations parallel those employed in Sect. C.1 for single-fluid-phase flow without species transport. The inclusion of species transport adds some more terms to the CEI. For completeness, we provide the details needed to assemble the CEI. The exposition follows the organization of Table 10.2, with groupings of lines in Eq. (10.14) considered in turn and relevant manipulations presented. Some terms that originate in a particular conservation, balance, or thermodynamic equation are distributed into various lines of the CEI. Origination equations for terms in Eq. (10.13) are indicated at the far right of that equation so they can be easily located.

Lines 1–5

Lines 1–5 of Eq. (10.14) are a collection of terms from the equations listed in Table 10.2 as they appear in Eq. (10.13). The quantities h^{α} and b^{α} for $\alpha \in \mathfrak{I}$ are moved directly from $\mathcal{E}_{**}^{\overline{\overline{w}}}$ and $\mathcal{S}_{**}^{\overline{\overline{w}}}$, respectively, to lines 1 and 3. Terms involving the material derivatives of $\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}}$ and of $\mu_{i\alpha} - \mu^{i\overline{\alpha}}$, for $\alpha \in \mathfrak{I}$ from $\mathcal{T}_{*}^{\overline{\overline{\alpha}}}$, can be found in lines 1–4. Material derivatives of $\psi^{i\overline{\alpha}}$, with $\alpha \in \mathfrak{I}$, are obtained from $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$. These material derivatives are found in lines 2 and 5. The remaining terms in lines 1–5 are obtained by manipulating some additional terms that originate in the energy and gravitational potential equations.

The material derivative terms involving $K_E^{\overline{\overline{i\alpha}}} + \mathbf{u}^{\overline{\overline{i\alpha}}} \cdot \mathbf{u}^{\overline{\overline{i\alpha}}}/2$ that appear in $\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$ are treated differently for each entity. For the w phase, apply identity Eq. (7.49) to obtain

$$\sum_{i\in\mathfrak{I}_s} \varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\frac{\mathrm{D}^{\overline{w}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{iw}}} + \frac{\mathbf{u}^{\overline{\overline{iw}}}\cdot\mathbf{u}^{\overline{\overline{iw}}}}{2}\right) = \underbrace{\left\langle \sum_{i\in\mathfrak{I}_s} \rho_w\omega_{iw}\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{iw}}} + \frac{\mathbf{u}^{\overline{\overline{iw}}}\cdot\mathbf{u}^{\overline{\overline{iw}}}}{2}\right)\right\rangle_{\Omega_w,\Omega}}_{2}$$

$$\underbrace{+\sum_{i\in\mathfrak{I}_s} \varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\nabla\left(K_E^{\overline{\overline{iw}}} + \frac{\mathbf{u}^{\overline{\overline{iw}}}\cdot\mathbf{u}^{\overline{\overline{iw}}}}{2}\right)}_{33}\cdot\underbrace{\left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}\right)}_{35}, \tag{C.40}$$

where an under-braced number indicates the line in Eq. (10.14) in which the denoted term appears.

For the solid phase, there is no need to change the reference velocity of the material derivative, so we have

$$\sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}}\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{is}}}+\frac{\mathbf{u}^{\overline{\overline{is}}}\cdot\mathbf{u}^{\overline{\overline{is}}}}{2}\right)=\underbrace{\left\langle \sum_{i\in\mathfrak{J}_s} \rho_s\omega_{is}\frac{\mathrm{D}^{\overline{s}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{is}}}+\frac{\mathbf{u}^{\overline{\overline{is}}}\cdot\mathbf{u}^{\overline{\overline{is}}}}{2}\right)\right\rangle_{\Omega_s,\Omega}}_{2} . \tag{C.41}$$

For the corresponding interface term from equation $\mathcal{E}_{**}^{\overline{\overline{ws}}}$, we first introduce the averaging operator to obtain

$$\begin{aligned}
&\sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\frac{\mathrm{D}^{\overline{ws}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\\
&\qquad=\sum_{i\in\mathfrak{J}_s}\left\langle \rho_{ws}\omega_{iws}\frac{\mathrm{D}^{\overline{ws}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\right\rangle_{\Omega_{ws},\Omega} .
\end{aligned} \tag{C.42}$$

We make use of Eq. (7.85), with $i\alpha$ and α replaced by ws, to modify the material derivative on the right side of Eq. (C.42) and obtain

$$\begin{aligned}
&\sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\frac{\mathrm{D}^{\overline{ws}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\\
&\quad=\sum_{i\in\mathfrak{J}_s}\left\langle \rho_{ws}\omega_{iws}\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\right\rangle_{\Omega_{ws},\Omega}\\
&\qquad+\sum_{i\in\mathfrak{J}_s}\left\langle \rho_{ws}\omega_{iws}(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}})\cdot\nabla\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\right\rangle_{\Omega_{ws},\Omega}\\
&\qquad-\sum_{i\in\mathfrak{J}_s}\left\langle \rho_{ws}\omega_{iws}(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})\cdot(\mathbf{I}-\mathbf{I}'_{ws})\cdot\nabla\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\right\rangle_{\Omega_{ws},\Omega} .
\end{aligned} \tag{C.43}$$

The last summation in this expression can be split into two summations by replacing $\mathbf{v}_{ws}-\mathbf{v}^{\overline{w}}$ with $(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}})+(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}})$. We then make use of the fact that macroscale quantities can be moved outside the averaging operator to obtain

$$\begin{aligned}
&\sum_{i\in\mathfrak{J}_s} \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\frac{\mathrm{D}^{\overline{ws}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\\
&\quad=\underbrace{\sum_{i\in\mathfrak{J}_s}\left\langle \rho_{ws}\omega_{iws}\frac{\mathrm{D}'^{\overline{s}}}{\mathrm{D}t}\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\right\rangle_{\Omega_{ws},\Omega}}_{4,5}\\
&\qquad+\underbrace{\sum_{i\in\mathfrak{J}_s}\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\nabla\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)}_{37}\cdot\underbrace{(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}})}_{42}
\end{aligned}$$

$$\underbrace{-\sum_{i\in\mathfrak{I}_s}\left\langle\rho_{ws}\omega_{iws}(\mathbf{v}_{ws}-\mathbf{v}^{\overline{ws}})\cdot(\mathbf{I}-\mathbf{l}'_{ws})\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)}_{49,50}$$

$$\underbrace{-\sum_{i\in\mathfrak{I}_s}\left\langle\rho_{ws}\omega_{iws}(\mathbf{I}-\mathbf{l}'_{ws})\right\rangle_{\Omega_{ws},\Omega}\cdot\nabla\left(K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\cdot(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}})}_{41,42}\ . \tag{C.44}$$

The remaining entries in lines 1–5 involve the material derivative of $\psi_{i\alpha}$. The antecedent terms are the partial time derivative from $\mathcal{G}_{**}^{\overline{\overline{\alpha}}}$ and the gravitational term from $\mathcal{P}_{**}^{\overline{\overline{\alpha}}}$. This pairing is considered separately for each entity. For the w phase, we can add the terms and add and subtract $\mathbf{v}^{\overline{s}}$ in the gravity portion of the sum, which provides

$$\left\langle\rho_w\omega_{iw}\frac{\partial\psi_{iw}}{\partial t}\right\rangle_{\Omega_w,\Omega}-\varepsilon^{\overline{\overline{w}}}\rho^w\omega^{i\overline{w}}\mathbf{g}^{\overline{iw}}\cdot\mathbf{v}^{\overline{w}}=\left\langle\rho_w\omega_{iw}\frac{\partial\psi_{iw}}{\partial t}\right\rangle_{\Omega_w,\Omega}$$
$$-\varepsilon^{\overline{\overline{w}}}\rho^w\omega^{i\overline{w}}\mathbf{g}^{\overline{iw}}\cdot\mathbf{v}^{\overline{s}}-\varepsilon^{\overline{\overline{w}}}\rho^w\omega^{i\overline{w}}\mathbf{g}^{\overline{iw}}\cdot(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}})\ . \tag{C.45}$$

Introduction of the averaging operator in the second term on the right side then gives

$$\left\langle\rho_w\omega_{iw}\frac{\partial\psi_{iw}}{\partial t}\right\rangle_{\Omega_w,\Omega}-\varepsilon^{\overline{\overline{w}}}\rho^w\omega^{i\overline{w}}\mathbf{g}^{\overline{iw}}\cdot\mathbf{v}^{\overline{w}}=\left\langle\rho_w\omega_{iw}\frac{\partial\psi_{iw}}{\partial t}\right\rangle_{\Omega_w,\Omega}$$
$$-\left\langle\rho_w\omega_{iw}\mathbf{g}_{iw}\cdot\mathbf{v}^{\overline{s}}\right\rangle_{\Omega_w,\Omega}-\varepsilon^{\overline{\overline{w}}}\rho^w\omega^{i\overline{w}}\mathbf{g}^{\overline{iw}}\cdot(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}})\ . \tag{C.46}$$

Because $\mathbf{g}_{i\alpha}+\nabla\psi_{i\alpha}=0$, the material derivative may be introduced so that we obtain

$$\left\langle\rho_w\omega_{iw}\frac{\partial\psi_{iw}}{\partial t}\right\rangle_{\Omega_w,\Omega}-\varepsilon^{\overline{\overline{w}}}\rho^w\omega^{i\overline{w}}\mathbf{g}^{\overline{iw}}\cdot\mathbf{v}^{\overline{w}}$$
$$=\underbrace{\left\langle\rho_w\omega_{iw}\frac{\mathrm{D}^{\overline{s}}\psi_{iw}}{\mathrm{D}t}\right\rangle_{\Omega_w,\Omega}}_{2}-\underbrace{\varepsilon^{\overline{\overline{w}}}\rho^w\omega^{i\overline{w}}\mathbf{g}^{\overline{iw}}}_{33}\cdot\underbrace{(\mathbf{v}^{\overline{w}}-\mathbf{v}^{\overline{s}})}_{35}\ . \tag{C.47}$$

For the s phase, the manipulations are similar; but because the velocity is already $\mathbf{v}^{\overline{s}}$, no relative velocity term arises. We obtain

$$\left\langle\rho_s\omega_{is}\frac{\partial\psi_{is}}{\partial t}\right\rangle_{\Omega_s,\Omega}-\varepsilon^{\overline{\overline{s}}}\rho^s\omega^{i\overline{s}}\mathbf{g}^{\overline{is}}\cdot\mathbf{v}^{\overline{s}}$$
$$=\left\langle\rho_s\omega_{is}\frac{\partial\psi_{is}}{\partial t}\right\rangle_{\Omega_s,\Omega}-\left\langle\rho_s\omega_{is}\mathbf{g}_{is}\cdot\mathbf{v}^{\overline{s}}\right\rangle_{\Omega_s,\Omega}=\underbrace{\left\langle\rho_s\omega_{is}\frac{\mathrm{D}^{\overline{s}}\psi_{is}}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}}_{2}\ . \tag{C.48}$$

For the *ws* interface, the manipulations are more involved. One term from $\mathcal{G}_{**}^{\overline{\overline{\alpha}}}$ and one from $\mathcal{P}_{**}^{\overline{\overline{\alpha}}}$ for $\alpha = ws$ are combined. Introduction of $\mathbf{v}^{\overline{s}}$ gives

$$\begin{aligned}
&\left\langle \rho_{ws}\omega_{iws}\left[\frac{\partial'\psi_{iws}}{\partial t} + \mathbf{v}_{iws}\cdot\left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws}\right]\right\rangle_{\Omega_{ws},\Omega} - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}\cdot\mathbf{v}^{\overline{ws}} \\
&\quad = \left\langle \rho_{ws}\omega_{iws}\left[\frac{\partial'\psi_{iws}}{\partial t} + \mathbf{v}_{iws}\cdot\left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws}\right]\right\rangle_{\Omega_{ws},\Omega} - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}\cdot\mathbf{v}^{\overline{s}} \\
&\qquad - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}\cdot\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) .
\end{aligned} \tag{C.49}$$

We express the second term on the right side in terms of the averaging operator over the interface, which yields

$$\begin{aligned}
&\left\langle \rho_{ws}\omega_{iws}\left[\frac{\partial'\psi_{iws}}{\partial t} + \mathbf{v}_{iws}\cdot\left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws}\right]\right\rangle_{\Omega_{ws},\Omega} - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}\cdot\mathbf{v}^{\overline{ws}} \\
&\quad = \left\langle \rho_{ws}\omega_{iws}\left[\frac{\partial'\psi_{iws}}{\partial t} + \mathbf{v}_{iws}\cdot\left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws} - \mathbf{g}_{iws}\cdot\mathbf{v}^{\overline{s}}\right]\right\rangle_{\Omega_{ws},\Omega} \\
&\qquad - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}\cdot\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) .
\end{aligned} \tag{C.50}$$

We will make use of the identity

$$\mathbf{g}_{iws} = -\nabla'\psi_{iws} + \left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws}, \tag{C.51}$$

so that Eq. (C.50) becomes

$$\begin{aligned}
&\left\langle \rho_{ws}\omega_{iws}\left[\frac{\partial'\psi_{iws}}{\partial t} + \mathbf{v}_{iws}\cdot\left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws}\right]\right\rangle_{\Omega_{ws},\Omega} - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}\cdot\mathbf{v}^{\overline{ws}} \\
&\quad = \left\langle \rho_{ws}\omega_{iws}\left[\frac{\partial'\psi_{iws}}{\partial t} + \mathbf{v}^{\overline{s}}\cdot\nabla'\psi_{iws} + \left(\mathbf{v}_{iws} - \mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws}\right]\right\rangle_{\Omega_{ws},\Omega} \\
&\qquad - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}\cdot\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}\right) .
\end{aligned} \tag{C.52}$$

The material derivative on the surface as defined in Eq. (7.84) is

$$\frac{\mathrm{D}^{\prime\overline{s}}}{\mathrm{D}t} = \frac{\partial'}{\partial t} + \mathbf{v}^{\overline{s}}\cdot\nabla' . \tag{C.53}$$

Insertion of this identity into Eq. (C.52) and noting that $\mathbf{v}_{iws}\cdot\left(\mathsf{I}-\mathsf{I}'\right) = \mathbf{v}_{ws}\cdot\left(\mathsf{I}-\mathsf{I}'\right)$ (because the interfacial species velocity normal to the interface is equal to the interface velocity) gives

$$\left\langle \rho_{ws}\omega_{iws}\left[\frac{\partial'\psi_{iws}}{\partial t} + \mathbf{v}_{iws}\cdot\left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws}\right]\right\rangle_{\Omega_{ws},\Omega} - \varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}\cdot\mathbf{v}^{\overline{ws}}$$

$$= \underbrace{\left\langle \rho_{ws}\omega_{iws}\frac{\mathrm{D}'^{\overline{s}}\psi_{iws}}{\mathrm{D}t}\right\rangle_{\Omega_{ws},\Omega}}_{4} + \underbrace{\left\langle \rho_{ws}\omega_{iws}(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})\cdot\left(\mathsf{I}-\mathsf{I}'\right)\cdot\mathbf{g}_{iws}\right\rangle_{\Omega_{ws},\Omega}}_{44}$$

$$- \underbrace{\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mathbf{g}^{\overline{iws}}}_{37}\underbrace{\cdot\left(\mathbf{v}^{\overline{ws}}-\mathbf{v}^{\overline{s}}\right)}_{42} \; . \tag{C.54}$$

Lines 6–10

Elements from $\mathcal{S}_{**}^{\overline{\overline{\alpha}}}$, $\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$, $\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$, $\mathcal{G}_{**}^{\overline{\overline{\alpha}}}$, and $\mathcal{T}_{*}^{\overline{\overline{s}}}$ can be manipulated using the product rule to yield the entries given in Lines 6–10 of Eq. (10.14). These terms involve entropy and heat fluxes—along with entries related to the divergence of deviation velocities and a solid-phase stress-deformation term. The required mathematical manipulations are application of the product rule and algebraic rearrangement.

The term $\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}\right)$ for $\alpha \in \Im$ is moved directly from $\mathcal{S}_{**}^{\overline{\overline{\alpha}}}$ to lines 6 and 8. The terms involving $\mathbf{q}^{\overline{\overline{\alpha}}}$ from $\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$ and $\mathbf{q}_{\mathbf{g}0}$ from $\mathcal{G}_{**}^{\overline{\overline{\alpha}}}$ can be combined and rearranged together according to

$$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}0}\right) = \underbrace{\nabla\cdot\left[\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}(\mathbf{q}^{\overline{\overline{\alpha}}}+\mathbf{q}_{\mathbf{g}0}\right]}_{6,8} - \underbrace{\varepsilon^{\overline{\overline{\alpha}}}(\mathbf{q}^{\overline{\overline{\alpha}}}+\mathbf{q}_{\mathbf{g}0})}_{13,15}\cdot\underbrace{\nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)}_{14,16} \; . \tag{C.55}$$

Next, consider the terms involving $\mathbf{u}^{\overline{\overline{i\alpha}}}$ associated with $\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$. We begin with the fact that, because the sum of $\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}$ over all species equals zero, the $\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}$ term may be dropped to yield

$$\sum_{i\in\Im_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{i\alpha}}+\psi^{\overline{i\alpha}}-\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right)$$

$$= \sum_{i\in\Im_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{i\alpha}}+\psi^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right) \; . \tag{C.56}$$

Selective application of the product rule to the quantities on the right side yields

$$\sum_{i\in\Im_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{i\alpha}}+\psi^{\overline{i\alpha}}-\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right)$$

$$= \underbrace{\nabla\cdot}_{6,8}\underbrace{\sum_{i\in\Im_s}\left[\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\mathbf{u}^{\overline{\overline{i\alpha}}}\right]}_{7,9}$$

$$\underbrace{-\sum_{i\in\mathfrak{I}_s}\left[\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\left(\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}\right)\mathbf{u}^{\overline{\overline{i\alpha}}}\right]\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)}_{14,15,16}$$
$$\underbrace{+\sum_{i\in\mathfrak{I}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\psi^{\overline{i\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\right)}_{\mathcal{G}_{**}^{\overline{\overline{\alpha}}}}$$
$$-\sum_{i\in\mathfrak{I}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\nabla\left(\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}+\psi^{\overline{i\alpha}}\right). \tag{C.57}$$

The term with an equation type beneath the underbrace cancels with the same term that is provided by the equation denoted. Therefore, this term does not appear in the CEI. The term on the right without an underbrace is modified additionally making use of the fact that

$$\sum_{i\in\mathfrak{I}_{s/N}}\omega^{i\overline{\alpha\beta}}\mathbf{u}^{\overline{\overline{i\alpha}}}=-\omega^{r\overline{\alpha}}\mathbf{u}^{\overline{\overline{N\alpha}}}, \tag{C.58}$$

where N is one of the species selected as a reference species. Substitution of this relation into the last term in Eq. (C.57) yields

$$-\sum_{i\in\mathfrak{I}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\nabla\left(\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}+\psi^{\overline{i\alpha}}\right)$$
$$=-\underbrace{\sum_{i\in\mathfrak{I}_{s/N}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\omega^{i\overline{\alpha}}\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\nabla\left[\mu^{\overline{i\alpha}}+K_E^{\overline{\overline{i\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{i\alpha}}}\cdot\mathbf{u}^{\overline{\overline{i\alpha}}}}{2}+\psi^{\overline{i\alpha}}\right.}_{17}$$
$$\left.\underbrace{-\left(\mu^{\overline{N\alpha}}+K_E^{\overline{\overline{N\alpha}}}+\frac{\mathbf{u}^{\overline{\overline{N\alpha}}}\cdot\mathbf{u}^{\overline{\overline{N\alpha}}}}{2}+\psi^{\overline{N\alpha}}\right)}_{18}\right]. \tag{C.59}$$

The remaining term needed for Lines 6–10 is associated with the solid phase and is derived by application of the product rule to a term originating in equation $\mathcal{T}_*^{\overline{\overline{s}}}$ such that

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla\cdot\left\langle\left(\mathbf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathsf{C}_s}{j_s}\mathsf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}$$
$$=\underbrace{-\nabla\cdot\left[\frac{1}{\theta^{\overline{\overline{s}}}}\right.}_{8}\underbrace{\left.\left\langle\left(\mathbf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathsf{C}_s}{j_s}\mathsf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]}_{10}$$

$$\underbrace{+\left\langle\left(\mathbf{t}_s-\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{s}}}}\right)}_{16}. \tag{C.60}$$

Lines 11 and 12

Lines 11 and 12 of Eq. (10.14) are products of fluxes and deformation rate tensor forces. As noted in Table 10.2, these terms originate in equations $\mathcal{S}_{**}^{\overline{\overline{\alpha}}}$, $\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$, $\boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}$, $\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$, $\mathcal{T}_{*}^{\overline{\overline{s}}}$, and $\mathcal{T}_{*}^{\overline{\overline{ws}}}$. For the most part, the terms in the CEI are obtained simply by collecting terms that multiply $\mathbf{d}^{\overline{\overline{\alpha}}}$ from all the equations combined into Eq. (9.32) and summing them.

There is one instance when the product rule must be employed in forming lines 11 and 12. The energy equation, $\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$, provides a term involving the stress tensor that can be expanded to obtain

$$\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}\right)=\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right)\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}{:}\left(\nabla\mathbf{v}^{\overline{\alpha}}\right)^{\mathrm{T}}. \tag{C.61}$$

Because $\mathbf{t}^{\overline{\overline{\alpha}}}$ is symmetric, this equation can be written as

$$\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}\right)=\underbrace{\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right)\cdot\mathbf{v}^{\overline{\alpha}}}_{\boldsymbol{\mathcal{P}}_{**}^{\overline{\overline{\alpha}}}}+\underbrace{\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}{:}\mathbf{d}^{\overline{\overline{\alpha}}}}_{11,12}, \tag{C.62}$$

where the first term on the right cancels with a like term originating from the momentum equation, while the second term survives and appears as indicated.

The next task is to look through Eq. (10.13) and collect all the other terms that multiply $\mathbf{d}^{\overline{\overline{w}}}$. Some of the multipliers cancel each other, but the terms that survive form the left side of the following equation:

$$-\left(E^{\overline{\overline{w}}}-\eta^{\overline{\overline{w}}}\theta^{\overline{\overline{w}}}-\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\mu^{\overline{iw}}\right)\mathbf{I}{:}\mathbf{d}^{\overline{\overline{w}}}=\underbrace{\varepsilon^{\overline{\overline{w}}}p^{w}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{w}}}}_{11}, \tag{C.63}$$

where the equality is obtained from the Euler equation for the w phase, Eq. (7.13) with $\alpha=w$,

$$E^{\overline{\overline{w}}}=\eta^{\overline{\overline{w}}}\theta^{\overline{\overline{w}}}-\varepsilon^{\overline{\overline{w}}}p^{w}+\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{w}}}\rho^{w}\omega^{i\overline{w}}\mu^{\overline{iw}}. \tag{C.64}$$

For the solid phase, the multipliers of $\mathbf{d}^{\overline{\overline{s}}}$ in Eq. (10.13) are collected to obtain the expression on the left side of the following equation:

$$-\left[\left(E^{\overline{\overline{s}}}-\eta^{\overline{\overline{s}}}\theta^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\frac{\mathbf{C}^s}{j^s}-\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{s}}}\rho^{s}\omega^{i\overline{s}}\mu^{\overline{is}}\right)\mathbf{I}+\mathbf{t}^s\right]{:}\mathbf{d}^{\overline{\overline{s}}}=-\underbrace{\mathbf{t}^s{:}\mathbf{d}^{\overline{\overline{s}}}}_{11}. \tag{C.65}$$

The quantity on the left in parentheses is equal to 0 according to the Euler equation for the solid, given as the fourth equation in Table 7.1, which gives the simplification obtained on the right.

For the *ws* entity, the terms that multiply $\mathbf{d}^{\overline{\overline{ws}}}$ in Eq. (10.13) are collected on the left side of the equation

$$
\begin{aligned}
&-\left[\left(E^{\overline{\overline{ws}}}-\eta^{\bar{\bar{s}}}\theta^{\overline{\overline{ws}}}-\sum_{i\in\mathfrak{I}_s}\varepsilon^{\overline{\overline{ws}}}\rho^{ws}\omega^{i\overline{ws}}\mu^{\overline{iws}}\right)\mathbf{I}-\left\langle(\mathbf{I}-\mathbf{I}'_\alpha)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}\right]:\mathbf{d}^{\overline{\overline{ws}}}\\
&\quad=-\underbrace{\left[\varepsilon^{\overline{\overline{ws}}}\gamma^{ws}\mathbf{I}-\left\langle(\mathbf{I}-\mathbf{I}'_\alpha)\gamma_{ws}\right\rangle_{\Omega_{ws},\Omega}\right]:\mathbf{d}^{\overline{\overline{ws}}}}_{12}\,. \qquad \text{(C.66)}
\end{aligned}
$$

The simplification on the right side of the equation makes use of the macroscale Euler equation for an interface, the sixth equation in Table 7.1, with α replaced by *ws*.

Lines 13–16

These lines have already been completed as collateral terms from the preceding development of lines 1–12. In particular, the terms in these lines were obtained as follows:

Line 13: Eq. (C.55);
Line 14: Eqs. (C.55) and (C.57);
Line 15: Eqs. (C.55) and (C.57); and
Line 16: Eqs. (C.55), (C.57), and (C.60).

Lines 17 and 18

These lines were also completed in the preceding derivation with the terms coming from Eq. (C.59).

Lines 19 and 20

These lines are a combination of terms that contain the reaction rate $r^{i\alpha}$. Part comes from $\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$ and the other part comes from $\mathcal{G}_{**}^{\overline{\overline{\alpha}}}$. Use is also made of the fact that since the sum of $r^{i\alpha}$ over all species is zero, the term involving the sum over all species of $r^{i\alpha}\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}/2$ is also zero.

Lines 21 and 22

These terms arise from $\mathcal{M}_{**}^{\overline{\overline{iw}}}$ and $\mathcal{M}_{**}^{\overline{\overline{iws}}}$. The terms extracted are on the left of the following equation, and they are rearranged on the right side such that

$$\begin{aligned}
&-\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{iw}}+\psi^{\overline{iw}}+K_E^{\overline{\overline{iw}}}+\frac{\mathbf{u}^{\overline{\overline{iw}}}\cdot\mathbf{u}^{\overline{\overline{iw}}}}{2}\right)\overset{iws\to iw}{M}\\
&\qquad-\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{iws}}+\psi^{\overline{iws}}+K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\overset{iw\to iws}{M}\\
&=\underbrace{\sum_{i\in\mathfrak{J}_s}\overset{iw\to iws}{M}\left[\frac{1}{\theta^{\overline{\overline{w}}}}\left(\mu^{\overline{iw}}+K_E^{\overline{\overline{iw}}}+\frac{\mathbf{u}^{\overline{\overline{iw}}}\cdot\mathbf{u}^{\overline{\overline{iw}}}}{2}+\psi^{\overline{iw}}\right)\right.}_{21}\\
&\qquad\underbrace{\left.-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{iws}}+K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}+\psi^{\overline{iws}}\right)\right]}_{22}\,.
\end{aligned}\tag{C.67}$$

Lines 23 and 24

This pair of lines is similar to lines 21 and 22 with the exception being that the s phase is considered rather than the w phase. These terms arise from $\mathcal{M}_{**}^{\overline{\overline{is}}}$ and $\mathcal{M}_{**}^{\overline{\overline{iws}}}$. The terms employed are on the left of the following equation, and they are rearranged on the right side such that

$$\begin{aligned}
&-\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{is}}+\psi^{\overline{is}}+K_E^{\overline{\overline{is}}}+\frac{\mathbf{u}^{\overline{\overline{is}}}\cdot\mathbf{u}^{\overline{\overline{is}}}}{2}\right)\overset{iws\to is}{M}\\
&\qquad-\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{iws}}+\psi^{\overline{iws}}+K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}\right)\overset{is\to iws}{M}\\
&=\underbrace{\sum_{i\in\mathfrak{J}_s}\overset{is\to iws}{M}\left[\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{is}}+K_E^{\overline{\overline{is}}}+\frac{\mathbf{u}^{\overline{\overline{is}}}\cdot\mathbf{u}^{\overline{\overline{is}}}}{2}+\psi^{\overline{is}}\right)\right.}_{23}\\
&\qquad\underbrace{\left.-\frac{1}{\theta^{\overline{\overline{ws}}}}\left(\mu^{\overline{iws}}+K_E^{\overline{\overline{iws}}}+\frac{\mathbf{u}^{\overline{\overline{iws}}}\cdot\mathbf{u}^{\overline{\overline{iws}}}}{2}+\psi^{\overline{iws}}\right)\right]}_{24}\,.
\end{aligned}\tag{C.68}$$

Additionally, the following identity is used to add and subtract terms to Eq. (10.14) in the lines indicated:

$$\sum_{i\in\mathfrak{J}_s} \underbrace{\overset{is\to iws}{M} \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^s}{3\rho^s j^s}}_{23} - \underbrace{\left\langle \frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}:\mathbf{C}^s}{3\rho^s j^s} \rho_s (\mathbf{v}_s - \mathbf{v}_{ws})\cdot\mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega}}_{25} = 0\,. \tag{C.69}$$

Line 25

One term has already been provided here from Eq. (C.69). A second term comes from $\mathcal{T}_*^{\overline{\overline{s}}}$ with

$$-\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot(\mathbf{v}_{ws} - \mathbf{v}_s)\,\boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{j_s} \right\rangle_{\Omega_{ws},\Omega} = \underbrace{\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \boldsymbol{\sigma}_s : \frac{\mathbf{C}_s}{\rho_s j_s} \rho_s (\mathbf{v}_s - \mathbf{v}_{ws})\cdot\mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega}}_{25} . \tag{C.70}$$

The other term in line 25 also originates in $\mathcal{T}_*^{\overline{\overline{s}}}$ but is obtained only after some rearrangement. The derivation begins by stating

$$\begin{aligned} -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot(\mathbf{v}_s - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega} = & -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot(\mathbf{v}_s - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega} \\ & -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws}\cdot(\mathbf{v}_s - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega} . \end{aligned} \tag{C.71}$$

The first term on the right side can be modified further by adding and subtracting $\mathbf{v}_{ws}$ to $\mathbf{v}_s - \mathbf{v}^{\overline{s}}$ and then multiplying and dividing by ρ_s to obtain

$$\begin{aligned} -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot(\mathbf{v}_s - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega} = & -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \frac{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s}{\rho_s} \rho_s (\mathbf{v}_s - \mathbf{v}_{ws})\cdot\mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega} \\ -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega} & - \frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws}\cdot(\mathbf{v}_s - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega} . \end{aligned} \tag{C.72}$$

The second term on the right side is modified by adding and subtracting $1/\theta^{\overline{\overline{ws}}}$ to and from $1/\theta^{\overline{\overline{s}}}$ so that we have

$$\begin{aligned} -\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot(\mathbf{v}_s - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega} = & \underbrace{-\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \frac{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s}{\rho_s} \rho_s (\mathbf{v}_s - \mathbf{v}_{ws})\cdot\mathbf{n}_s \right\rangle_{\Omega_{ws},\Omega}}_{25} \\ \underbrace{-\frac{1}{\theta^{\overline{\overline{ws}}}}}_{43} \left\langle \underbrace{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s}_{43} \underbrace{\cdot(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}})}_{44} \right\rangle_{\Omega_{ws},\Omega} & \underbrace{-\frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_{ws}\cdot(\mathbf{v}_s - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega}}_{45} \\ \underbrace{-\left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}}\right) \left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot(\mathbf{v}_{ws} - \mathbf{v}^{\overline{s}}) \right\rangle_{\Omega_{ws},\Omega}}_{31} & . \end{aligned} \tag{C.73}$$

Lines 26–28, 29–31

The terms in lines 26–28 and 29–31 of Eq. (10.14) are descriptive of energy exchanges between the w and ws entities and between the s and ws entities, respectively. One term that appears in line 31 has been obtained in Eq. (C.73). A second term that involves p_w is obtained from $\mathcal{T}_*^{\overline{\overline{w}}}$ with the following manipulation:

$$\begin{aligned}\frac{1}{\theta^{\overline{\overline{w}}}}\left\langle \mathbf{n}_w\cdot(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})p_w\right\rangle_{\Omega_{ws},\Omega} &= \underbrace{\left(\frac{1}{\theta^{\overline{\overline{w}}}}-\frac{1}{\theta^{\overline{\overline{ws}}}}\right)\left\langle \mathbf{n}_w\cdot(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})p_w\right\rangle_{\Omega_{ws},\Omega}}_{28} \\ &\quad + \underbrace{\frac{1}{\theta^{\overline{\overline{ws}}}}\left\langle \mathbf{n}_w\cdot(\mathbf{v}_{ws}-\mathbf{v}^{\overline{s}})p_w\right\rangle_{\Omega_{ws},\Omega}}_{43,44} .\end{aligned} \tag{C.74}$$

The antecedent terms for the remaining elements of these lines and several others are all the terms in Eq. (10.13) involving inter-entity exchanges except those that have already been deployed into lines 21–24. For convenience, we will denote this collection of terms as X. These terms originate in $\mathcal{E}_{**}^{\overline{\overline{\alpha}}}$, $\mathcal{P}_{**}^{\overline{\overline{\alpha}}}$, $\mathcal{M}_{**}^{\overline{\overline{i\alpha}}}$, and $\mathcal{G}_{**}^{\overline{\overline{\alpha}}}$ for $\alpha \in \mathfrak{I}$. The terms of interest are

$$\begin{aligned} X = {} & \sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\sum_{i\in\mathfrak{I}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}+\frac{\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)}{2}+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}\right] \\ & +\sum_{\alpha\in\mathfrak{I}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\overset{\kappa\to\alpha}{Q_1}\right] \\ & -\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\sum_{i\in\mathfrak{I}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\mathbf{v}^{\overline{\alpha}}-\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\mathbf{v}^{\overline{\alpha}}\cdot\overset{\kappa\to\alpha}{\mathbf{T}_0} \\ & +\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\sum_{i\in\mathfrak{I}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\right)\overset{i\kappa\to i\alpha}{M} \\ & +\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\sum_{i\in\mathfrak{I}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\psi_i^{\overline{\overline{\alpha,\kappa}}}+\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\overset{\kappa\to\alpha}{G_0} .\end{aligned} \tag{C.75}$$

In Eq. (C.75), the terms are listed in the order in which they appear in Eq. (10.13). The bulk of the work to be done to obtain the specific terms that appear in lines 26–31 involves rearranging Eq. (C.75) so that all velocities are relative to $\mathbf{v}^{\overline{s}}$. We therefore first rearrange the terms so that those involving products of velocity with mass exchange are the last terms in the listing:

$$\begin{aligned} X = {} & \sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\overset{\kappa\to\alpha}{Q_1}+\overset{\kappa\to\alpha}{G_0}\right) \\ & +\sum_{\alpha\in\mathfrak{I}}\sum_{\kappa\in\mathfrak{I}_{c\alpha}}\sum_{i\in\mathfrak{I}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}+\psi_i^{\overline{\overline{\alpha,\kappa}}}\right]\end{aligned}$$

$$
\begin{aligned}
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\mathbf{v}^{\overline{\alpha}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left[\frac{\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)}{2}\right]\\
&-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}\right)\cdot\mathbf{v}^{\overline{\alpha}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}\right)\,. \qquad \text{(C.76)}
\end{aligned}
$$

The last three groups of summations are readily condensed so that we have

$$
\begin{aligned}
X=&\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\overset{\kappa\to\alpha}{Q_1}+\overset{\kappa\to\alpha}{G_0}\right)\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}+\psi_i^{\overline{\overline{\alpha,\kappa}}}\right]\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\mathbf{v}^{\overline{\alpha}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left[\frac{\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{\alpha}}\right)\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{\alpha}}\right)}{2}\right]\,. \\
&\qquad \text{(C.77)}
\end{aligned}
$$

With the equation in this form, we can subtract $\mathbf{v}^{\overline{s}}$ from each velocity, since this reference velocity will cancel out of the equation, to obtain

$$
\begin{aligned}
X=&\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\overset{\kappa\to\alpha}{Q_1}+\overset{\kappa\to\alpha}{G_0}\right)\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}}+K_{Ei}^{\overline{\overline{\alpha,\kappa}}}+\psi_i^{\overline{\overline{\alpha,\kappa}}}\right]\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{\kappa\to\alpha}{\mathbf{T}_0}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\sum_{i\in\mathfrak{J}_s}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\overset{i\kappa\to i\alpha}{M}\frac{1}{2}\left\{\left[\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)-\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\right]\right.\\
&\qquad\left.\cdot\left[\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}+\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)-\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\right]\right\}\,. \qquad \text{(C.78)}
\end{aligned}
$$

The group of terms in the last summation now can be expanded, making sure to keep the velocities relative to the solid phase velocity rather than canceling out $\mathbf{v}^{\overline{s}}$.

After this expansion, the terms are grouped to obtain

$$\begin{aligned} X = & \sum_{\alpha\in\mathfrak{J}} \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left(\overset{\kappa\to\alpha}{Q_1} + \overset{\kappa\to\alpha}{G_0} \right) \\ & + \sum_{\alpha\in\mathfrak{J}} \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \sum_{i\in\mathfrak{J}_s} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \overset{i\kappa\to i\alpha}{M} \left[\overline{E}_i^{\overline{\overline{\alpha,\kappa}}} + K_{Ei}^{\overline{\overline{\alpha,\kappa}}} + \frac{\mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}} \cdot \mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}}}{2} + \psi_i^{\overline{\overline{\alpha,\kappa}}} \right] \\ & + \sum_{\alpha\in\mathfrak{J}} \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left[\overset{\kappa\to\alpha}{\mathbf{T}_0} + \sum_{i\in\mathfrak{J}_s} \overset{i\kappa\to i\alpha}{M} \left(\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}}}{2} + \mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}} \right) \right] \cdot \left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}} \right) \\ & - \sum_{\alpha\in\mathfrak{J}} \sum_{\kappa\in\mathfrak{J}_{c\alpha}} \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\{ \overset{\kappa\to\alpha}{\mathbf{T}_0} - \sum_{i\in\mathfrak{J}_s} \overset{i\kappa\to i\alpha}{M} \left[\frac{\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}}{2} - \left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}} - \mathbf{v}^{\overline{s}} + \mathbf{u}_i^{\overline{\overline{\alpha,\kappa}}} \right) \right] \right\} \\ & \qquad \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right) . \end{aligned} \tag{C.79}$$

The derivation is completed by expanding out the summations over α and κ. Also, all the exchange terms are written so that the transfer is from the *w* and *s* phases to the interface (i.e., the negative of a transfer from the interface to a phase). Expansion of the summations then yields

$$\begin{aligned} X = & - \Bigg\{ \underbrace{\overset{w\to ws}{Q_1} + \overset{w\to ws}{G_0} + \sum_{i\in\mathfrak{J}_s} \left(\overline{E}_{iw}^{\overline{ws}} + K_{Eiw}^{\overline{\overline{ws}}} + \frac{\mathbf{u}_{iw}^{\overline{\overline{ws}}} \cdot \mathbf{u}_{iw}^{\overline{\overline{ws}}}}{2} + \psi_{iw}^{\overline{ws}} \right) \overset{iw\to iws}{M}}_{26} \\ & \underbrace{+ \left[\overset{w\to ws}{\mathbf{T}_0} + \sum_{i\in\mathfrak{J}_s} \left(\frac{\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} + \mathbf{u}_{iw}^{\overline{\overline{ws}}} \right) \overset{iw\to iws}{M} \right] \cdot \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)}_{27} \Bigg\} \underbrace{\left(\frac{1}{\theta^{\overline{\overline{w}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right)}_{28} \\ & - \Bigg\{ \underbrace{\overset{s\to ws}{Q_1} + \overset{s\to ws}{G_0} + \sum_{i\in\mathfrak{J}_s} \left(\overline{E}_{is}^{\overline{ws}} + K_{Eis}^{\overline{\overline{ws}}} + \frac{\mathbf{u}_{is}^{\overline{\overline{ws}}} \cdot \mathbf{u}_{is}^{\overline{\overline{ws}}}}{2} + \psi_{is}^{\overline{ws}} \right) \overset{is\to iws}{M}}_{29} \\ & \underbrace{+ \left[\overset{s\to ws}{\mathbf{T}_0} + \sum_{i\in\mathfrak{J}_s} \left(\frac{\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} + \mathbf{u}_{is}^{\overline{\overline{ws}}} \right) \overset{is\to iws}{M} \right] \cdot \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\overline{s}} \right)}_{30} \Bigg\} \underbrace{\left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{ws}}}} \right)}_{31} \\ & \underbrace{+ \frac{1}{\theta^{\overline{\overline{w}}}} \left\{ \overset{w\to ws}{\mathbf{T}_0} - \sum_{i\in\mathfrak{J}_s} \overset{iw\to iws}{M} \left[\frac{\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}}}{2} - \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} + \mathbf{u}_{iw}^{\overline{\overline{ws}}} \right) \right] \right\} \cdot \left(\mathbf{v}^{\overline{w}} - \mathbf{v}^{\overline{s}} \right)}_{34,35} \\ & \underbrace{- \frac{1}{\theta^{\overline{\overline{ws}}}} \left\{ \overset{w\to ws}{\mathbf{T}_0} - \sum_{i\in\mathfrak{J}_s} \overset{iw\to iws}{M} \left[\frac{\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\overline{s}}}{2} - \left(\mathbf{v}_w^{\overline{ws}} - \mathbf{v}^{\overline{s}} + \mathbf{u}_{iw}^{\overline{\overline{ws}}} \right) \right] \right.}_{38} \end{aligned}$$

$$\underbrace{+\overset{s\to ws}{\mathbf{T}_0} - \sum_{i\in\mathfrak{I}_s} \overset{is\to iws}{M} \left[\frac{\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\bar{s}}}{2} - \left(\mathbf{v}_s^{\overline{ws}} - \mathbf{v}^{\bar{s}} + \mathbf{u}_{is}^{\overline{\overline{ws}}}\right)\right]}_{39} \Bigg\} \cdot \underbrace{\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\bar{s}}\right)}_{42} . \tag{C.80}$$

Lines 32–35

Some of these terms have already been obtained from Eqs. (C.40), (C.47), and (C.80). The remaining terms transfer directly from $\mathcal{T}_*^{\overline{\overline{w}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{w}}}$. They are the parts of these equations that multiply $\mathbf{v}^{\bar{w}} - \mathbf{v}^{\bar{s}}$.

Lines 36–42

Many of these terms have already been obtained from Eqs. (C.44), (C.54), and (C.80). A few terms transfer directly from the parts of $\mathcal{T}_*^{\overline{\overline{ws}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$ that multiply $\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\bar{s}}$. Additional terms that appear in these lines are obtained from rearrangement of contributions from $\mathcal{T}_*^{\overline{\overline{ws}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}}$. The terms extracted from these forms are the left side of the following equation, and the rearrangements on the right result from replacing $\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}$ with $(\mathbf{v}_{ws} - \mathbf{v}^{\overline{ws}}) + (\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\bar{s}})$ in each term. The result is

$$\begin{aligned}
&\frac{1}{\theta^{\overline{\overline{ws}}}} \left\langle \eta_{ws}\left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega} \cdot \nabla\theta^{\overline{\overline{ws}}} \\
&\quad + \frac{1}{\theta^{\overline{\overline{ws}}}} \sum_{i\in\mathfrak{I}_s} \left\langle \rho_{ws}\omega_{iws}\left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega} \cdot \nabla\mu^{\overline{iws}} \\
&\quad + \frac{1}{\theta^{\overline{\overline{ws}}}} \sum_{i\in\mathfrak{I}_s} \left\langle \rho_{ws}\omega_{iws}\left(\mathbf{v}_{ws} - \mathbf{v}^{\bar{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega} \cdot \nabla\psi^{\overline{iws}} \\
&= \underbrace{\frac{1}{\theta^{\overline{\overline{ws}}}} \left\langle \eta_{ws}\left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{ws}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega} \cdot \nabla\theta^{\overline{\overline{ws}}}}_{47} \\
&\quad + \underbrace{\frac{1}{\theta^{\overline{\overline{ws}}}}}_{36} \underbrace{\left[\left\langle \eta_{ws}\left(\mathsf{I} - \mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega} \cdot \nabla\theta^{\overline{\overline{ws}}}\right]}_{40} \cdot \underbrace{\left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\bar{s}}\right)}_{42} \\
&\quad \underbrace{+ \frac{1}{\theta^{\overline{\overline{ws}}}} \sum_{i\in\mathfrak{I}_s} \left\langle \rho_{ws}\omega_{iws}\left(\mathbf{v}_{ws} - \mathbf{v}^{\overline{ws}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega} \cdot \nabla\left(\mu^{\overline{iws}} + \psi^{\overline{iws}}\right)}_{49,50} \\
&\quad + \underbrace{\frac{1}{\theta^{\overline{\overline{ws}}}}}_{36} \underbrace{\left[\sum_{i\in\mathfrak{I}_s} \left\langle \rho_{ws}\omega_{iws}\left(\mathsf{I} - \mathsf{I}'_{ws}\right)\right\rangle_{\Omega_{ws},\Omega} \cdot \nabla\left(\mu^{\overline{iws}} + \psi^{\overline{iws}}\right)\right] \cdot \left(\mathbf{v}^{\overline{ws}} - \mathbf{v}^{\bar{s}}\right)}_{41,42} .
\end{aligned} \tag{C.81}$$

Line 43 and 44

Three contributions to these lines have been made as byproducts of other manipulations according to Eqs. (C.54), (C.73), and (C.74). Additionally, the term involving γ_{ws} is acquired directly from $\mathcal{T}_*^{\overline{\overline{ws}}}$.

Lines 45–50

These lines have been produced, for the most part, from the manipulations to obtain terms for the preceding lines. The origins of these lines are as follows:

Line 45: Eq. (C.73);
Line 46: This is obtained directly from $\mathcal{T}_*^{\overline{\overline{s}}}$;
Line 47: Eq. (C.81);
Line 48: This is obtained directly from $\mathcal{T}_*^{\overline{\overline{ws}}}$;
Lines 49 and 50: Eqs. (C.44) and (C.81).

C.3 CEI for Two-fluid-phase Flow, Eq. (11.5)

In this section, the manipulations that lead to the CEI for two-fluid-phase flow in porous media are presented. The starting point is Eq. (11.4). This equation is the entropy inequality augmented by conservation and thermodynamic equations for the fluid phases, the solid phase, the interfaces, and the common curve with values for the Lagrange multipliers selected. The particular forms of the conservation equations used to augment the entropy inequality are the entity-based, material derivative forms available in Table 6.3. The thermodynamic equations are the entity based forms referenced in Table 7.2. We will consider the case where only the solid phase can sustain a concentrated force at the common curve so that the singularities for the fluid phases are zero. If the designated equations are substituted into Eq. (11.4) and the material time derivatives are cancelled, the resulting equation is

$$\begin{aligned}
&\sum_{\alpha\in\mathfrak{J}}\Bigg[\eta^{\overline{\overline{\alpha}}}\mathbf{l}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}b^{\alpha}-\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{\kappa\to\alpha}{M}\,\overline{\eta}^{\overline{\overline{\alpha,\kappa}}}-\sum_{\kappa\in\mathfrak{J}_{c\alpha}}\overset{\kappa\to\alpha}{\Phi} && \mathcal{S}_*^{\overline{\overline{\alpha}}}\\
&\qquad\qquad-\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\boldsymbol{\varphi}^{\overline{\overline{\alpha}}}\right)\Bigg] && \mathcal{S}_*^{\overline{\overline{\alpha}}}\\
&-\overset{wns\to s}{\Phi^*}+\overset{wns\to s}{\Phi^*} && \mathcal{S}_*^{\overline{\overline{s}}},\mathcal{S}_*^{\overline{\overline{wns}}}\\
&-\sum_{\alpha\in\mathfrak{J}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\frac{\mathrm{D}^{\overline{\alpha}}K_E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}+\left[E^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left(\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_E^{\overline{\overline{\alpha}}}\right)\right]\mathbf{l}{:}\mathbf{d}^{\overline{\overline{\alpha}}}\right\} && \mathcal{E}_*^{\overline{\overline{\alpha}}}
\end{aligned}$$

$$+\sum_{\alpha\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}h^{\alpha}\right)\qquad\mathcal{E}_{*}^{\overline{\overline{\alpha}}}$$

$$+\sum_{\alpha\in\mathcal{J}}\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\overline{\alpha,\kappa}}}}+\frac{\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}}\cdot\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}}}{2}+K_{E}^{\overline{\overline{\overline{\alpha,\kappa}}}}\right)\qquad\mathcal{E}_{*}^{\overline{\overline{\alpha}}}$$

$$+\sum_{\alpha\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{\mathbf{T}}\cdot\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}}+\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{Q}\right]\qquad\mathcal{E}_{*}^{\overline{\overline{\alpha}}}$$

$$+\sum_{\alpha\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}\right)\qquad\mathcal{E}_{*}^{\overline{\overline{\alpha}}}$$

$$+\left(\overset{wns\to s}{\mathbf{T}^{*}}\cdot\mathbf{v}_{s}^{\overline{wns}}+\overset{wns\to s}{Q^{*}}\right)\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\right)\qquad\mathcal{E}_{*}^{\overline{\overline{s}}},\mathcal{E}_{*}^{\overline{\overline{wns}}}$$

$$+\sum_{\alpha\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\mathbf{v}^{\overline{\alpha}}\cdot\left[\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}-\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{M}\mathbf{v}^{\overline{\overline{\overline{\alpha,\kappa}}}}\right]\qquad\boldsymbol{\mathcal{P}}_{*}^{\overline{\overline{\alpha}}}$$

$$-\sum_{\alpha\in\mathcal{J}}\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\mathbf{v}^{\overline{\alpha}}\cdot\overset{\kappa\to\alpha}{\mathbf{T}}-\sum_{\alpha\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\mathbf{v}^{\overline{\alpha}}\cdot\left[\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right)\right]\qquad\boldsymbol{\mathcal{P}}_{*}^{\overline{\overline{\alpha}}}$$

$$-\overset{wns\to s}{\mathbf{T}^{*}}\cdot\left(\frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}}-\frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{\overline{wns}}}}}\right)\qquad\boldsymbol{\mathcal{P}}_{*}^{\overline{\overline{s}}},\boldsymbol{\mathcal{P}}_{*}^{\overline{\overline{wns}}}$$

$$+\sum_{\alpha\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}-\frac{\mathbf{v}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}}{2}+K_{E}^{\overline{\overline{\alpha}}}\right)\qquad\mathcal{M}_{*}^{\overline{\overline{\alpha}}}$$

$$\times\left(\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}-\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}}\overset{\kappa\to\alpha}{M}\right)\qquad\mathcal{M}_{*}^{\overline{\overline{\alpha}}}$$

$$-\sum_{\alpha\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\Psi^{\overline{\overline{\alpha}}}\mathsf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}}+\varepsilon^{\overline{\overline{\alpha}}}h^{\overline{\overline{\alpha}}}\right]\qquad\mathcal{G}_{*}^{\overline{\overline{\alpha}}}$$

$$+\sum_{\alpha\in\mathcal{J}}\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\overset{\kappa\to\alpha}{M}\psi^{\overline{\overline{\overline{\alpha,\kappa}}}}+\overset{\kappa\to\alpha}{G}+\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}_{\mathbf{g}}^{\overline{\overline{\alpha}}}\right)\right]\qquad\mathcal{G}_{*}^{\overline{\overline{\alpha}}}$$

$$+\sum_{\alpha\in\mathcal{J}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left\langle\rho_{\alpha}\left[\frac{\partial^{(n)}\psi_{\alpha}}{\partial t}+\mathbf{v}_{\alpha}\cdot\left(\mathsf{I}-\mathsf{I}_{\alpha}^{(n)}\right)\cdot\mathbf{g}_{\alpha}\right]\right\rangle_{\Omega_{\alpha},\Omega}\qquad\mathcal{G}_{*}^{\overline{\overline{\alpha}}}$$

$$+\sum_{\alpha\in\mathcal{J}_{\mathrm{f}}}\sum_{\kappa\in\mathcal{J}_{\mathrm{c}\alpha}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left\langle\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{s}}\right)p_{\alpha}\right\rangle_{\Omega_{\kappa},\Omega}\qquad\mathcal{T}_{*}^{\overline{\overline{w}}},\mathcal{T}_{*}^{\overline{\overline{n}}}$$

$$+\sum_{\alpha\in\mathcal{J}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\left\langle\eta_{\alpha}\frac{\mathrm{D}^{\overline{s}}(\theta_{\alpha}-\theta^{\overline{\overline{\alpha}}})}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}\right.\qquad\mathcal{T}_{*}^{\overline{\overline{w}}},\mathcal{T}_{*}^{\overline{\overline{n}}}$$

$$\left.+\left\langle\rho_{\alpha}\frac{\mathrm{D}^{\overline{s}}\left(\mu_{\alpha}-\mu^{\overline{\alpha}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}\right]\qquad\mathcal{T}_{*}^{\overline{\overline{w}}},\mathcal{T}_{*}^{\overline{\overline{n}}}$$

$$-\sum_{\alpha\in\mathcal{J}_{\mathrm{f}}}\frac{1}{\theta^{\overline{\overline{\overline{\alpha}}}}}\left[\eta^{\overline{\overline{\alpha}}}\nabla\theta^{\overline{\overline{\alpha}}}-\nabla(\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha})+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\mu^{\overline{\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\qquad\mathcal{T}_{*}^{\overline{\overline{w}}},\mathcal{T}_{*}^{\overline{\overline{n}}}$$

$$-\sum_{\kappa\in\mathfrak{J}_{\mathrm{cs}}}\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot(\mathbf{v}_\kappa-\mathbf{v}_s)\,\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Omega_\kappa,\Omega}\qquad\mathcal{T}_*^{\overline{\overline{s}}}$$

$$-\sum_{\kappa\in\mathfrak{J}_{\mathrm{cs}}}\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_\kappa,\Omega}+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\eta_s\frac{\mathrm{D}^{\overline{s}}(\theta_s-\theta^{\overline{\overline{s}}})}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}\qquad\mathcal{T}_*^{\overline{\overline{s}}}$$

$$+\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\rho_s\frac{\mathrm{D}^{\overline{s}}(\mu_s-\mu^{\overline{s}})}{\mathrm{D}t}\right\rangle_{\Omega_s,\Omega}\qquad\mathcal{T}_*^{\overline{\overline{s}}}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla\cdot\left\langle\left[\mathbf{t}_s-\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\mathbf{I}\right]\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\qquad\mathcal{T}_*^{\overline{\overline{s}}}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left[\varepsilon^{\overline{\overline{s}}}\mathbf{t}^s:\mathbf{d}^{\overline{\overline{s}}}-\varepsilon^{\overline{\overline{s}}}\boldsymbol{\sigma}^{\overline{\overline{s}}}:\frac{\mathbf{C}^s}{j^s}\mathbf{I}:\mathbf{d}^{\overline{\overline{s}}}\right.\qquad\mathcal{T}_*^{\overline{\overline{s}}}$$

$$\left.-\left\langle\left(\nabla\cdot\mathbf{t}_s-\nabla\boldsymbol{\sigma}_s:\frac{\mathbf{C}_s}{j_s}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]\qquad\mathcal{T}_*^{\overline{\overline{s}}}$$

$$-\frac{1}{\theta^{\overline{\overline{s}}}}\left[\left\langle\mathbf{n}_s\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\boldsymbol{\sigma}_s^*:\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Omega_{wns},\Omega}+\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}\right]\qquad\mathcal{T}_*^{\overline{\overline{s}}}$$

$$-\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\mathbf{n}_\alpha\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha\right\rangle_{\Omega_{wns},\Omega}\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left\langle\eta_\alpha\frac{\mathrm{D}^{\prime\overline{s}}(\theta_\alpha-\theta^{\overline{\overline{\alpha}}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}\right.\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$\left.+\left\langle\rho_\alpha\frac{\mathrm{D}^{\prime\overline{s}}(\mu_\alpha-\mu^{\overline{\alpha}})}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}\right]\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$-\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\eta^{\overline{\overline{\alpha}}}\nabla\theta^{\overline{\overline{\alpha}}}+\nabla\cdot\left\langle\mathbf{I}'_\alpha\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}+\varepsilon^{\overline{\overline{\alpha}}}\rho^\alpha\nabla\mu^{\overline{\alpha}}\right]\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\right.\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$\left.+\left\langle\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}:\mathbf{d}^{\overline{\overline{\alpha}}}\right]\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\nabla'\cdot\mathbf{I}'_\alpha\cdot\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\eta_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}}\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$+\sum_{\alpha\in\mathfrak{J}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\mu^{\overline{\alpha}}\qquad\mathcal{T}_*^{\overline{\overline{wn}}},\mathcal{T}_*^{\overline{\overline{ws}}},\mathcal{T}_*^{\overline{\overline{ns}}}$$

$$+\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left\langle\eta_{wns}\frac{\mathrm{D}^{\prime\prime\overline{s}}(\theta_{wns}-\theta^{\overline{\overline{wns}}})}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}\qquad\mathcal{T}_*^{\overline{\overline{\overline{wns}}}}$$

$$
\begin{aligned}
&+\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left\langle \rho_{wns}\frac{\mathrm{D}''^{\overline{s}}(\mu_{wns}-\mu^{\overline{wns}})}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega} && \mathcal{T}_{*}^{\overline{\overline{\overline{wns}}}}\\
&-\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\Big[\eta^{\overline{\overline{wns}}}\nabla\theta^{\overline{\overline{wns}}}-\nabla\cdot\left\langle \mathbf{I}''_{\alpha}\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega} && \mathcal{T}_{*}^{\overline{\overline{\overline{wns}}}}\\
&\qquad\qquad +\varepsilon^{\overline{\overline{wns}}}\rho^{wns}\nabla\mu^{\overline{wns}}\Big]\cdot\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right) && \mathcal{T}_{*}^{\overline{\overline{\overline{wns}}}}\\
&+\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left[\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\right] && \mathcal{T}_{*}^{\overline{\overline{\overline{wns}}}}\\
&-\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left[\left\langle\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}:\mathbf{d}^{\overline{\overline{wns}}}\right] && \mathcal{T}_{*}^{\overline{\overline{\overline{wns}}}}\\
&-\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left\langle\nabla''\cdot\mathbf{I}''_{wns}\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega} && \mathcal{T}_{*}^{\overline{\overline{\overline{wns}}}}\\
&+\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left\langle\eta_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\theta^{\overline{\overline{wns}}} && \mathcal{T}_{*}^{\overline{\overline{\overline{wns}}}}\\
&+\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left\langle\rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\mu^{\overline{wns}} && \mathcal{T}_{*}^{\overline{\overline{\overline{wns}}}}\\
&-\sum_{\alpha\in\mathfrak{I}_{\mathrm{P}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left\langle\rho_{\alpha}\frac{\mathrm{D}^{\overline{s}}\psi^{\overline{\alpha}}}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\cdot\nabla\psi^{\overline{\alpha}}\right] && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{w}}},\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{n}}},\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{s}}}\\
&-\sum_{\alpha\in\mathfrak{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left[\left\langle\rho_{\alpha}\frac{\mathrm{D}'^{\overline{s}}\psi^{\overline{\alpha}}}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}+\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla\psi^{\overline{\alpha}}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\right] && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{wn}}},\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}},\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ns}}}\\
&+\sum_{\alpha\in\mathfrak{I}_{\mathrm{I}}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\rho_{\alpha}\left(\mathbf{v}_{\alpha}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}'_{\alpha}\right)\right\rangle_{\Omega_{\alpha},\Omega}\cdot\nabla\psi^{\overline{\alpha}} && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{wn}}},\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ws}}},\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{ns}}}\\
&-\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left[\left\langle\rho_{wns}\frac{\mathrm{D}''^{\overline{s}}\psi^{\overline{wns}}}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}+\varepsilon^{\overline{\overline{wns}}}\rho^{wns}\nabla\psi^{\overline{wns}}\cdot\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)\right] && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\overline{wns}}}}\\
&+\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}\left\langle\rho_{wns}\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathbf{I}-\mathbf{I}''_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla\psi^{\overline{wns}} && \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\overline{wns}}}}\\
&=\sum_{\alpha\in\mathfrak{I}}\Lambda^{\overline{\overline{\alpha}}}\geq 0\,. && \mathcal{S}_{**}^{\overline{\overline{\alpha}}}
\end{aligned}
\tag{C.82}
$$

No rearrangement of terms has been carried out, and the equations that are the sources of the various lines in this equation are indicated in the right margin.

Simplification of the EI given by Eq. (C.82) to the final form CEI, Eq. (11.5), requires manipulations of the sort encountered for the single-fluid-phase application as provided in Sect. C.1. For the present application, the addition of one fluid phase, two interfaces, and a common curve increases the complexity of the manipulations needed to derive the desired CEI. On the other hand, the manipulations needed are similar in type. Therefore, without compromising completeness or clarity, and in the interest of conciseness, we will provide the steps of the assembly from the lines in Eq. (C.82) to Eq. (11.5) while referring to similar formulation steps already considered. When the need for manipulations not already considered arises, for example in the treatment of the common curve, the steps are provided. Table C.1 provides a listing of the lines in Eq. (11.5) and the equations that contribute elements to these lines.

The exchange of entropy among entities for the two-fluid-phase system consists of the exchange terms from $\mathcal{S}_*^{\overline{\overline{\alpha}}}$. The two terms relating to concentrated sources are equal and opposite in sign. The remaining terms accounting for exchanges due to phase change and non-advective transport must also cancel such that

$$\sum_{\alpha\in\mathfrak{J}}\ \sum_{\kappa\in\mathfrak{J}_{\mathrm{c}\alpha}} \left(\overset{\kappa\to\alpha}{M}\ \overline{\eta}^{\overline{\overline{\alpha,\kappa}}} + \overset{\kappa\to\alpha}{\Phi} \right) = 0\,. \tag{C.83}$$

Thus, these terms do not appear in the CEI. This simplification occurs because the terms detailed in Eq. (C.83) only transfer entropy from one entity to another and do not affect the total entropy generation rate in the system. Although the exchange terms for mass, momentum, energy, and body force potential also cancel if the corresponding conservation equations are summed over all entities, they remain in the CEI because they are summed only after multiplication by a Lagrange multiplier that is different for each entity. Thus, closure relations can be obtained for these other exchange terms from the CEI.

Lines 1–6

These lines are similar to lines 1–4 of the single-fluid-phase CEI given in Eq. (9.43). The quantities h^{α} and b^{α} for $\alpha \in \mathfrak{J}$ are moved to lines 1, 3, and 5 for the phases, interfaces, and common curve, respectively, from $\mathcal{E}_*^{\overline{\overline{\alpha}}}$ and $\mathcal{S}_*^{\overline{\overline{\alpha}}}$. Terms involving the material derivatives of $\theta_{\alpha} - \theta^{\overline{\overline{\alpha}}}$ and $\mu_{\alpha} - \mu^{\overline{\alpha}}$ are moved directly from the thermodynamic equations $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ into lines 1–6. Likewise, material derivatives of $\psi^{\overline{\alpha}}$ are moved into lines 2, 4, and 6 from the $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$ equation. Obtaining the remaining terms in lines 1–6 requires some rearrangement of terms that appear in Eq. (C.82).

For the fluid phases, the material derivatives of $K_E^{\overline{\overline{\alpha}}}$ appear in $\mathcal{E}_*^{\overline{\overline{\alpha}}}$ and are rearranged as in Eq. (C.1) to obtain

$$\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\frac{\mathrm{D}^{\overline{\alpha}}K_E^{\overline{\overline{\alpha}}}}{\mathrm{D}t} = \underbrace{\left\langle \rho_{\alpha}\frac{\mathrm{D}^{\overline{s}}K_E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}\right\rangle_{\Omega_{\alpha},\Omega}}_{2} \underbrace{+\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla K_E^{\overline{\overline{\alpha}}}}_{29}\cdot\underbrace{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)}_{30} \quad \text{for } \alpha\in\mathfrak{J}_{\mathrm{f}}\,, \tag{C.84}$$

where an under-braced number corresponds to the line number in Eq. (11.5) in which the denoted term appears. For the solid phase, the result is as in Eq. (C.2) with

$$\epsilon^{\overline{\overline{s}}}\rho^{s}\frac{\mathrm{D}^{\overline{s}}K_E^{\overline{\overline{s}}}}{\mathrm{D}t} = \underbrace{\left\langle \rho_{s}\frac{\mathrm{D}^{\overline{s}}K_E^{\overline{\overline{s}}}}{\mathrm{D}t}\right\rangle_{\Omega_{s},\Omega}}_{2}\,. \tag{C.85}$$

Table C.1 CEI formulation summary for the derivation of Eq. (11.5), where the operation abbreviations represent A for addition and subtraction, E for Euler equation identity, I for identity tensor components, O for objective form, and P for the product rule; and the general entity qualifier α implies all entities unless otherwise noted

Line(s)	Force	Precursor Equation(s)	Operations
1–6	—	$\mathcal{S}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$	O,A
7–8	—	$\mathcal{S}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{s}}}$	P
9–11	$\mathbf{d}^{\overline{\overline{\alpha}}}$	$\mathcal{S}_*^{\overline{\overline{\alpha}}}, \mathcal{M}_*^{\overline{\overline{\alpha}}}, \mathcal{P}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{\alpha}}}$	E,P
12–13	$\nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)$	$\mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{s}}}$	P
14	$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right) - \frac{1}{\theta^{\overline{\overline{\kappa}}}}\left(\mu^{\overline{\kappa}} + K_E^{\overline{\overline{\kappa}}} + \psi^{\overline{\kappa}}\right)$	$\mathcal{M}_*^{\overline{\overline{\alpha}}}, \mathcal{M}_*^{\overline{\overline{\kappa}}}$ for $\alpha \in \mathcal{J}_{\mathrm{f}}, \kappa \in \mathcal{J}_{\mathrm{c}\alpha}^-$	—
15	$\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{s}} + K_E^{\overline{\overline{s}}} + \psi^{\overline{s}} + \frac{\sigma^{\overline{\overline{s}}}:\mathbf{C}^s}{3\rho^s j^s}\right) - \frac{1}{\theta^{\overline{\overline{\kappa}}}}\left(\mu^{\overline{\kappa}} + K_E^{\overline{\overline{\kappa}}} + \psi^{\overline{\kappa}}\right)$	$\mathcal{M}_*^{\overline{\overline{s}}}, \mathcal{M}_*^{\overline{\overline{\kappa}}}$ for $\kappa \in \mathcal{J}_{\mathrm{cs}}^-$	A
16	—	$\mathcal{T}_*^{\overline{\overline{s}}}$ for $\alpha \in \mathcal{J}, \kappa \in \mathcal{J}_{\mathrm{c}\alpha}^-$	A,I
17	$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}} + K_E^{\overline{\overline{\alpha}}} + \psi^{\overline{\alpha}}\right) - \frac{1}{\theta^{\overline{\overline{wns}}}}\left(\mu^{\overline{wns}} + K_E^{\overline{\overline{wns}}} + \psi^{\overline{wns}}\right)$	$\mathcal{M}_*^{\overline{\overline{\alpha}}}, \mathcal{M}_*^{\overline{\overline{wns}}}$ for $\alpha \in \mathcal{J}_{\mathrm{I}}$	—
18–26	$\frac{1}{\theta^{\overline{\overline{\alpha}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}}$	$\mathcal{M}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{\alpha}}}, \kappa \in \mathcal{J}_{\mathrm{c}\alpha}^-$	A,O
27–28	$\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}}$	$\mathcal{E}_*^{\overline{\overline{s}}}, \mathcal{E}_*^{\overline{\overline{wns}}}, \mathcal{P}_*^{\overline{\overline{s}}}, \mathcal{P}_*^{\overline{\overline{wns}}}, \mathcal{T}_*^{\overline{\overline{s}}}$	A,O
29–41	$\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}$	$\mathcal{M}_*^{\overline{\overline{\alpha}}}, \mathcal{P}_*^{\overline{\overline{\alpha}}}, \mathcal{E}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_*^{\overline{\overline{\alpha}}}, \mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$	A,O
42–49	—	$\mathcal{T}_*^{\overline{\overline{\alpha}}}, \mathcal{G}_*^{\overline{\overline{\kappa}}}$ for $\kappa \in \mathcal{J}_{\mathrm{c}\alpha}^-$	A,O
50–51	—	$\mathcal{E}_*^{\overline{\overline{s}}}, \mathcal{E}_*^{\overline{\overline{wns}}}, \mathcal{T}_*^{\overline{\overline{s}}}$	A,I
52	—	$\mathcal{T}_*^{\overline{\overline{s}}}$	—
53–58	—	$\mathcal{T}_*^{\overline{\overline{\alpha}}},$ for $\alpha \in \mathcal{J}_{\mathrm{I}} \cup \mathcal{J}_{\mathrm{C}}$	A,O
59	—	$\mathcal{S}_*^{\overline{\overline{\alpha}}}$	—

The material derivative of the interface property $K_E^{\overline{\overline{\alpha}}}$ from the energy equation $\mathcal{E}_*^{\overline{\overline{\alpha}}}$ for $\alpha \in \mathcal{J}_{\mathrm{I}}$ is rearranged analogously to Eqs. (C.3)–(C.5) such that we obtain

$$\begin{aligned}\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\frac{\mathrm{D}^{\overline{\alpha}}K_E^{\overline{\overline{\alpha}}}}{\mathrm{D}t} = & \underbrace{\left\langle \rho_\alpha \frac{\mathrm{D}'^{\overline{s}}K_E^{\overline{\overline{\alpha}}}}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}}_{4} + \underbrace{\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\nabla K_E^{\overline{\overline{\alpha}}}}_{31}\cdot\underbrace{(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}})}_{35} \\ & - \underbrace{\left\langle \rho_\alpha(\mathbf{v}_\alpha-\mathbf{v}^{\overline{\alpha}})\cdot(\mathsf{I}-\mathsf{I}'_\alpha)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla K_E^{\overline{\overline{\alpha}}}}_{55} \\ & - \underbrace{\left\langle \rho_\alpha(\mathsf{I}-\mathsf{I}'_\alpha)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla K_E^{\overline{\overline{\alpha}}}\cdot(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}})}_{35} \quad \text{for } \alpha\in\mathcal{J}_{\mathrm{I}}\,. \qquad \text{(C.86)}\end{aligned}$$

For the material derivative of the common curve property $K_E^{\overline{\overline{wns}}}$ that appears in $\mathcal{E}_*^{\overline{\overline{wns}}}$, the rearrangement is analogous to that employed for an interface property. First, we introduce the averaging operator to obtain

$$\epsilon^{\overline{\overline{wns}}}\rho^{wns}\frac{\mathrm{D}^{\overline{wns}}K_E^{\overline{\overline{wns}}}}{\mathrm{D}t} = \left\langle \rho_{wns}\frac{\mathrm{D}^{\overline{wns}}K_E^{\overline{\overline{wns}}}}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}\,. \qquad \text{(C.87)}$$

We then introduce the identity provided by Eq. (7.99), with α and $i\alpha$ replaced by *wns*, to the right side to obtain the expanded form

$$\begin{aligned}\epsilon^{\overline{\overline{wns}}}\rho^{wns}\frac{\mathrm{D}^{\overline{wns}}K_E^{\overline{\overline{wns}}}}{\mathrm{D}t} = & \underbrace{\left\langle \rho_{wns}\frac{\mathrm{D}''^{\overline{s}}K_E^{\overline{\overline{wns}}}}{\mathrm{D}t}\right\rangle_{\Omega_{wns},\Omega}}_{6} + \underbrace{\epsilon^{\overline{\overline{wns}}}\rho^{wns}\nabla K_E^{\overline{\overline{wns}}}}_{37}\cdot\underbrace{(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}})}_{41} \\ & - \underbrace{\left\langle \rho_{wns}(\mathbf{v}_{wns}-\mathbf{v}^{\overline{wns}})\cdot(\mathsf{I}-\mathsf{I}''_{wns})\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla K_E^{\overline{\overline{wns}}}}_{58} \\ & - \underbrace{\left\langle \rho_{wns}(\mathsf{I}-\mathsf{I}''_{wns})\right\rangle_{\Omega_{wns},\Omega}\cdot\nabla K_E^{\overline{\overline{wns}}}}_{40}\cdot\underbrace{(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}})}_{41}\,. \qquad \text{(C.88)}\end{aligned}$$

The remaining entries in lines 1–6 are the averages of terms involving material derivatives of ψ_α. These are most easily obtained by examining a combination of the partial time derivative and the gravitational terms originating in $\mathcal{G}_*^{\overline{\overline{\alpha}}}$. These manipulations were previously performed for a fluid phase, a solid phase, and an interface. The results apply here as well. For the fluid phases, based on Eq. (C.8), we have

$$\left\langle \rho_\alpha\frac{\partial\psi_\alpha}{\partial t}\right\rangle_{\Omega_\alpha,\Omega} - \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\cdot\mathbf{v}^{\overline{\alpha}} = \underbrace{\left\langle \rho_\alpha\frac{\mathrm{D}^{\overline{s}}\psi_\alpha}{\mathrm{D}t}\right\rangle_{\Omega_\alpha,\Omega}}_{2} - \underbrace{\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}}_{29}\cdot\underbrace{(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}})}_{30}$$

$$\text{for } \alpha\in\mathcal{J}_{\mathrm{f}}\,. \qquad \text{(C.89)}$$

For the solid phase, from Eq. (C.9), we have

$$\left\langle \rho_s \frac{\partial \psi_s}{\partial t} \right\rangle_{\Omega_s,\Omega} - \varepsilon^{\overline{\overline{s}}} \rho^s \mathbf{g}^{\overline{s}} \cdot \mathbf{v}^{\overline{s}} = \underbrace{\left\langle \rho_s \frac{\mathrm{D}^{\overline{s}} \psi_s}{\mathrm{D}t} \right\rangle_{\Omega_s,\Omega}}_{2} . \tag{C.90}$$

The derivation of the interface expressions corresponds to Eqs. (C.10)–(C.15) such that, for interface α rather than just for interface *ws*,

$$\begin{aligned} &\left\langle \rho_\alpha \left[\frac{\partial' \psi_\alpha}{\partial t} + \mathbf{v}_\alpha \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha \right) \cdot \mathbf{g}_\alpha \right] \right\rangle_{\Omega_\alpha,\Omega} - \varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{g}^{\overline{\alpha}} \cdot \mathbf{v}^{\overline{\alpha}} \\ &= \underbrace{\left\langle \rho_\alpha \frac{\mathrm{D}'^{\overline{s}} \psi_\alpha}{\mathrm{D}t} \right\rangle_{\Omega_\alpha,\Omega}}_{4} + \underbrace{\left\langle \rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}^{\overline{s}}) \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha \right) \cdot \mathbf{g}_\alpha \right\rangle_{\Omega_\alpha,\Omega}}_{43,45,47} \\ &\quad - \underbrace{\varepsilon^{\overline{\overline{\alpha}}} \rho^\alpha \mathbf{g}^{\overline{\alpha}}}_{32} \cdot \underbrace{(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}})}_{35} \quad \text{for } \alpha \in \mathfrak{I}_\mathrm{I} . \end{aligned} \tag{C.91}$$

For the common curve, the derivation is similar to that used for the interfaces. In fact, the derivations are identical if one replaces the single prime denoting a surface with the double prime indicating that one is concerned with the direction of a curve. Given the experience with this reality from the previous sections of the text, we simply write down the result based on inspection of Eq. (C.91) as

$$\begin{aligned} &\left\langle \rho_{wns} \left[\frac{\partial'' \psi_{wns}}{\partial t} + \mathbf{v}_{wns} \cdot \left(\mathsf{I} - \mathsf{I}''_{wns} \right) \cdot \mathbf{g}_{wns} \right] \right\rangle_{\Omega_{wns},\Omega} - \varepsilon^{\overline{\overline{wns}}} \rho^{wns} \mathbf{g}^{\overline{wns}} \cdot \mathbf{v}^{\overline{wns}} \\ &= \underbrace{\left\langle \rho_{wns} \frac{\mathrm{D}''^{\overline{s}} \psi_{wns}}{\mathrm{D}t} \right\rangle_{\Omega_{wns},\Omega}}_{6} + \underbrace{\left\langle \rho_{wns} (\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}) \cdot \left(\mathsf{I} - \mathsf{I}''_{wns} \right) \cdot \mathbf{g}_{wns} \right\rangle_{\Omega_{wns},\Omega}}_{49} \\ &\quad - \underbrace{\varepsilon^{\overline{\overline{wns}}} \rho^{wns} \mathbf{g}^{\overline{wns}}}_{37} \cdot \underbrace{(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}})}_{41} . \end{aligned} \tag{C.92}$$

Lines 7 and 8

Contributions from $\mathcal{S}_*^{\overline{\overline{\alpha}}}$, $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, $\mathcal{G}_*^{\overline{\overline{\alpha}}}$, and $\mathcal{T}_*^{\overline{\overline{s}}}$ are employed to provide the elements of lines 7 and 8 of the CEI. Construction of the terms requires application of the product rule.

The non-advective entropy flux, $\nabla\cdot(\varepsilon^{\overline{\overline{\alpha}}} \varphi^{\overline{\overline{\alpha}}})$ for $\alpha \in \mathfrak{I}$, is taken from $\mathcal{S}_*^{\overline{\overline{\alpha}}}$ and inserted into line 7 for all entities except the solid and into line 8 for the solid. The divergences of the non-advective heat flux $\nabla\cdot(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}^{\overline{\overline{\alpha}}})$ and the mechanical flux $\nabla\cdot(\varepsilon^{\overline{\overline{\alpha}}} \mathbf{q}_\mathbf{g}^{\overline{\overline{\alpha}}})$ are found in $\mathcal{E}_*^{\overline{\overline{\alpha}}}$ and $\mathcal{G}_*^{\overline{\overline{\alpha}}}$, respectively. They can be combined and rearranged using the product rule to obtain

$$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q}^{\overline{\overline{\alpha}}}+\varepsilon^{\overline{\overline{\alpha}}}\mathbf{q_g}\right)=\underbrace{\nabla\cdot\left[\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}(\mathbf{q}^{\overline{\overline{\alpha}}}+\mathbf{q_g}\right]}_{7,8}\underbrace{-\varepsilon^{\overline{\overline{\alpha}}}(\mathbf{q}^{\overline{\overline{\alpha}}}+\mathbf{q_g})\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}\right)}_{12,13}\,. \tag{C.93}$$

The remaining term needed for line 8 makes use of the product rule applied to a term taken from $\mathcal{T}_*^{\overline{\overline{s}}}$ such that

$$\begin{aligned}&-\frac{1}{\theta^{\overline{\overline{s}}}}\nabla\cdot\left\langle\left(\mathbf{t}_s-\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\dot{j}_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\\&=\underbrace{-\nabla\cdot\left[\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\left(\mathbf{t}_s-\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\dot{j}_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\right]}_{8}\\&\quad\underbrace{+\left\langle\left(\mathbf{t}_s-\frac{\boldsymbol{\sigma}_s{:}\mathbf{C}_s}{\dot{j}_s}\mathbf{I}\right)\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_s,\Omega}\cdot\nabla\left(\frac{1}{\theta^{\overline{\overline{s}}}}\right)}_{13}\,.\end{aligned} \tag{C.94}$$

Lines 9–11

Lines 9–11 of Eq. (11.5) arise from equations $\mathcal{S}_*^{\overline{\overline{\alpha}}}$, $\mathcal{M}_*^{\overline{\overline{\alpha}}}$, $\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$, $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, and $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ for $\alpha\in\mathcal{I}$, as noted in Table C.1. In fact, there are no contributing terms in $\mathcal{T}_*^{\overline{\overline{w}}}$ or $\mathcal{T}_*^{\overline{\overline{n}}}$.

As was determined in Eq. (C.19), the terms arising from $\mathcal{E}_*^{\overline{\overline{\alpha}}}$ are rearranged using the product rule such that

$$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\cdot\mathbf{v}^{\overline{\alpha}}\right)=\underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}\nabla\cdot\left(\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}\right)\cdot\mathbf{v}^{\overline{\alpha}}}_{\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}}+\underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}\mathbf{t}^{\overline{\overline{\alpha}}}{:}\mathbf{d}^{\overline{\overline{\alpha}}}}_{9,10,11}\quad\text{for }\alpha\in\mathcal{I}\,. \tag{C.95}$$

The term with the underbrace designated $\boldsymbol{\mathcal{P}}_*^{\overline{\overline{\alpha}}}$ cancels with an identical term from the momentum equation and thus is not transferred to the CEI.

The remaining terms in Eq. (C.82) that multiply $\mathbf{d}^{\overline{\overline{\alpha}}}$ for $\alpha\in\mathcal{I}$ are now collected for lines 9–11 of Eq. (11.5). The contributions for the phases and interfaces are the same as were obtained for the single-fluid-phase CEI, so we merely list those results here. For the fluid phases, see Eq. (C.20), which—for the two fluid phases here—may be written as

$$-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(E^{\overline{\overline{\alpha}}}-\eta^{\overline{\overline{\alpha}}}\theta^{\overline{\overline{\alpha}}}-\varepsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mu^{\overline{\alpha}}\right)\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}=\underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}\varepsilon^{\overline{\overline{\alpha}}}p^{\alpha}\mathbf{I}{:}\mathbf{d}^{\overline{\overline{\alpha}}}}_{6}\quad\text{for }\alpha\in\mathcal{I}_{\mathrm{f}}\,. \tag{C.96}$$

The result for the solid phase is identical to Eq. (C.22),

$$-\frac{1}{\theta^{\bar{\bar{s}}}}\left[\left(E^{\bar{\bar{s}}}-\eta^{\bar{\bar{s}}}\theta^{\bar{\bar{s}}}-\varepsilon^{\bar{\bar{s}}}\boldsymbol{\sigma}^{\bar{\bar{s}}}:\frac{\mathbf{C}^s}{j^s}-\varepsilon^{\bar{\bar{s}}}\rho^s\mu^{\bar{s}}\right)\mathbf{I}+\varepsilon^{\bar{\bar{s}}}\mathbf{t}^s\right]:\mathbf{d}^{\bar{\bar{s}}}=-\underbrace{\frac{1}{\theta^{\bar{\bar{s}}}}\varepsilon^{\bar{\bar{s}}}\mathbf{t}^s:\mathbf{d}^{\bar{\bar{s}}}}_{9}\ . \tag{C.97}$$

For the interfaces, the result obtained in Eq. (C.23) applies and is

$$\begin{aligned}&-\frac{1}{\theta^{\bar{\bar{\alpha}}}}\left[\left(E^{\bar{\bar{\alpha}}}-\eta^{\bar{\bar{\alpha}}}\theta^{\bar{\bar{\alpha}}}-\varepsilon^{\bar{\bar{\alpha}}}\rho^\alpha\mu^{\bar{\alpha}}\right)\mathbf{I}-\left\langle(\mathbf{I}-\mathbf{I}'_\alpha)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\right]:\mathbf{d}^{\bar{\bar{\alpha}}}\\&=-\underbrace{\frac{1}{\theta^{\bar{\bar{\alpha}}}}\left[\varepsilon^{\bar{\bar{\alpha}}}\gamma^\alpha\mathbf{I}-\left\langle(\mathbf{I}-\mathbf{I}'_\alpha)\gamma_\alpha\right\rangle_{\Omega_\alpha,\Omega}\right]:\mathbf{d}^{\bar{\bar{\alpha}}}}_{10}\quad\text{for }\alpha\in\mathcal{J}_{\mathrm{I}}\ .\end{aligned} \tag{C.98}$$

The terms for the *wns* common curve that multiply $\mathbf{d}^{\overline{\overline{wns}}}$ are collected from Eq. (C.82) to form the left side of the following equation:

$$\begin{aligned}&-\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\left(E^{\overline{\overline{wns}}}-\eta^{\overline{\overline{wns}}}\theta^{\overline{\overline{wns}}}-\varepsilon^{\overline{\overline{wns}}}\rho^{wns}\mu^{\overline{wns}}\right)\mathbf{I}+\left\langle(\mathbf{I}-\mathbf{I}''_{wns})\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\right]:\mathbf{d}^{\overline{\overline{wns}}}\\&=\underbrace{\frac{1}{\theta^{\overline{\overline{wns}}}}\left[\varepsilon^{\overline{\overline{wns}}}\gamma^{wns}\mathbf{I}-\left\langle(\mathbf{I}-\mathbf{I}''_{wns})\gamma_{wns}\right\rangle_{\Omega_{wns},\Omega}\right]:\mathbf{d}^{\overline{\overline{wns}}}}_{11}\ .\end{aligned} \tag{C.99}$$

To obtain the right side of Eq. (C.99), use was made of the Euler equation for common curve thermodynamics, the last equation in Table 7.1.

Lines 12 and 13

The terms in these lines have been obtained as a byproduct of the production of lines 7 and 8. The terms are indicated in Eqs. (C.93) and (C.94).

Line 14

These terms arise from $\mathcal{M}_*^{\bar{\bar{\alpha}}}$ and $\mathcal{M}_*^{\bar{\bar{\kappa}}}$ for $\alpha\in\mathcal{J}$ and $\kappa\in\mathcal{J}_{\mathrm{c}\alpha}$. The terms are obtained via a simple rearrangement as in Eq. (C.24) such that

$$\begin{aligned}&-\frac{1}{\theta^{\bar{\bar{\alpha}}}}\left(\mu^{\bar{\alpha}}+\psi^{\bar{\alpha}}+K_E^{\bar{\bar{\alpha}}}\right)\overset{\kappa\to\alpha}{M}-\frac{1}{\theta^{\bar{\bar{\kappa}}}}\left(\mu^{\bar{\kappa}}+\psi^{\bar{\kappa}}+K_E^{\bar{\bar{\kappa}}}\right)\overset{\alpha\to\kappa}{M}\\&=\underbrace{\overset{\alpha\to\kappa}{M}\left[\frac{1}{\theta^{\bar{\bar{\alpha}}}}\left(\mu^{\bar{\alpha}}+K_E^{\bar{\bar{\alpha}}}+\psi^{\bar{\alpha}}\right)-\frac{1}{\theta^{\bar{\bar{\kappa}}}}\left(\mu^{\bar{\kappa}}+K_E^{\bar{\bar{\kappa}}}+\psi^{\bar{\kappa}}\right)\right]}_{14}\\&\qquad\qquad\text{for }\alpha\in\mathcal{J}_{\mathrm{f}},\kappa\in\mathcal{J}_{\mathrm{c}\alpha}\ ,\end{aligned} \tag{C.100}$$

where use has been made of the fact that $\overset{\alpha\to\kappa}{M}=-\overset{\kappa\to\alpha}{M}$.

Line 15

This line is similar to line 14 with the solid phase mass exchange with its connected entities being of interest. The equation is obtained from $\mathcal{M}_*^{\overline{\overline{s}}}$ and $\mathcal{M}_*^{\overline{\overline{\kappa}}}$ for $\kappa \in \mathcal{J}_{\mathrm{cs}}$. The equation is a generalization of Eq. (C.25) to the case where there is more than one member of the connected set of the s phase with

$$\begin{aligned} -\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{s}}+\psi^{\overline{s}}+K_E^{\overline{\overline{s}}}\right)\overset{\kappa\to s}{M}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\left(\mu^{\overline{\kappa}}+\psi^{\overline{\kappa}}+K_E^{\overline{\overline{\kappa}}}\right)\overset{s\to\kappa}{M} \\ =\underbrace{\overset{s\to\kappa}{M}\left[\frac{1}{\theta^{\overline{\overline{s}}}}\left(\mu^{\overline{s}}+K_E^{\overline{\overline{s}}}+\psi^{\overline{s}}\right)-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\left(\mu^{\overline{\kappa}}+K_E^{\overline{\overline{\kappa}}}+\psi^{\overline{\kappa}}\right)\right]}_{15} \\ \text{for } \kappa\in\mathcal{J}_{\mathrm{cs}}\,. \end{aligned} \tag{C.101}$$

The following identity is employed to add and subtract terms in Eq. (11.5),

$$\underbrace{\frac{1}{\theta^{\overline{\overline{s}}}}\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^s}{3\rho^s j^s}\overset{s\to\kappa}{M}}_{15}\underbrace{-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\frac{\boldsymbol{\sigma}^{\overline{\overline{s}}}{:}\mathbf{C}^s}{3\rho^s j^s}\rho_s(\mathbf{v}_s-\mathbf{v}_\kappa)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}}_{16}=0 \quad \text{for } \kappa\in\mathcal{J}_{\mathrm{cs}}\,. \tag{C.102}$$

Line 16

A term in addition to that provided from Eq. (C.102) comes from $\mathcal{T}_*^{\overline{\overline{s}}}$ with

$$\begin{aligned} -\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot(\mathbf{v}_\kappa-\mathbf{v}_s)\,\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{j_s}\right\rangle_{\Omega_\kappa,\Omega}=\underbrace{\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\boldsymbol{\sigma}_s{:}\frac{\mathbf{C}_s}{\rho_s j_s}\rho_s(\mathbf{v}_s-\mathbf{v}_\kappa)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}}_{16} \\ \text{for } \kappa\in\mathcal{J}_{\mathrm{cs}}\,. \end{aligned} \tag{C.103}$$

The other term in line 16 originates in $\mathcal{T}_*^{\overline{\overline{s}}}$. The rearrangement follows that presented for the single-fluid-phase case in Eqs. (C.28)–(C.31). The result for both the *ws* and *ns* interfaces is the same as that in Eq. (C.31) with

$$\begin{aligned} -\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_\kappa,\Omega}=\underbrace{-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\frac{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s}{\rho_s}\rho_s(\mathbf{v}_s-\mathbf{v}_\kappa)\cdot\mathbf{n}_s\right\rangle_{\Omega_\kappa,\Omega}}_{16} \\ -\underbrace{\frac{1}{\theta^{\overline{\overline{\kappa}}}}}_{44,46}\left\langle\underbrace{\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s}_{44,46}\cdot\underbrace{(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}})}_{45,47}\right\rangle_{\Omega_\kappa,\Omega}\underbrace{-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{l}'_\kappa\cdot(\mathbf{v}_s-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_\kappa,\Omega}}_{51} \end{aligned}$$

$$\underbrace{-\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\left\langle \mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s\mathbf{n}_s\cdot(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}})\right\rangle_{\Omega_\kappa,\Omega}}_{23} \quad \text{for } \kappa\in\mathfrak{I}_{\mathrm{cs}}\,. \qquad \text{(C.104)}$$

Line 17

These terms are mass exchanges between the interfaces and the common curve that originate in $\mathcal{M}_*^{\overline{\overline{\alpha}}}$ and $\mathcal{M}_*^{\overline{\overline{wns}}}$ for $\alpha\in\mathfrak{I}_{\mathrm{cwns}}^+$. The terms are obtained via a simple rearrangement of the terms collected from Eq. (C.82) such that

$$-\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}\right)\overset{wns\to\alpha}{M}-\frac{1}{\theta^{\overline{\overline{wns}}}}\left(\mu^{\overline{wns}}+\psi^{\overline{wns}}+K_E^{\overline{\overline{wns}}}\right)\overset{\alpha\to wns}{M}$$
$$=\underbrace{\overset{\alpha\to wns}{M}\left[\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left(\mu^{\overline{\alpha}}+K_E^{\overline{\overline{\alpha}}}+\psi^{\overline{\alpha}}\right)-\frac{1}{\theta^{\overline{\overline{wns}}}}\left(\mu^{\overline{wns}}+K_E^{\overline{\overline{wns}}}+\psi^{\overline{wns}}\right)\right]}_{17}$$
$$\text{for } \alpha\in\mathfrak{I}_{\mathrm{I}}\,. \qquad \text{(C.105)}$$

Lines 18–20, 21–23, and 24–26

These three sets of lines account for energy exchanges between the fluid phases and their boundaries, the solid phase and its boundaries, and the interfaces with the common curve, respectively. The derivation of the forms of these terms is virtually identical to that employed for the single-fluid-phase system in Eqs. (C.32)–(C.38), with the only difference being the need to account for the presence of the common curve. Thus, the derivation here will be abbreviated with deference to the earlier derivation for additional details.

From the derivation relating to line 16, one term was developed in Eq. (C.104) that has gone into line 23. An additional term involving p_α for $\alpha\in\mathfrak{I}_{\mathrm{f}}$ is obtained from $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ similarly to Eq. (C.32),

$$\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle \mathbf{n}_\alpha\cdot(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}})p_\alpha\right\rangle_{\Omega_\kappa,\Omega}=\underbrace{\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}-\frac{1}{\theta^{\overline{\overline{\kappa}}}}\right)\left\langle \mathbf{n}_\alpha\cdot(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}})p_\alpha\right\rangle_{\Omega_\kappa,\Omega}}_{20}$$
$$+\underbrace{\frac{1}{\theta^{\overline{\overline{\kappa}}}}\left\langle \mathbf{n}_\alpha\cdot(\mathbf{v}_\kappa-\mathbf{v}^{\overline{s}})p_\alpha\right\rangle_{\Omega_\kappa,\Omega}}_{42,44,46} \quad \text{for } \alpha\in\mathfrak{I}_{\mathrm{f}},\kappa\in\mathfrak{I}_{\mathrm{cf}}\,. \qquad \text{(C.106)}$$

A similar term for the interfacial tension is obtained from $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ for $\alpha\in\mathfrak{I}_{\mathrm{I}}$ where averaging is performed over the common curve. This expression is

$$\begin{aligned}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle \mathbf{n}_\alpha\cdot(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}})\gamma_\alpha\right\rangle_{\Omega_{wns},\Omega} &= \underbrace{\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)\left\langle \mathbf{n}_\alpha\cdot(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}})\gamma_\alpha\right\rangle_{\Omega_{wns},\Omega}}_{26} \\ &+ \underbrace{\frac{1}{\theta^{\overline{\overline{wns}}}}\left\langle \mathbf{n}_\alpha\cdot(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}})\gamma_\alpha\right\rangle_{\Omega_{wns},\Omega}}_{48,49} \quad \text{for } \alpha\in\mathcal{J}_\mathrm{I}\,. \end{aligned} \tag{C.107}$$

The remaining terms in lines 18–26 arise from the terms in Eq. (C.82) that account for inter-entity exchanges and which have not already been employed in lines 14, 15, and 17. The terms originate in $\mathcal{E}_*^{\overline{\overline{\alpha}}}$, $\mathcal{P}_*^{\overline{\overline{\alpha}}}$, $\mathcal{M}_*^{\overline{\overline{\alpha}}}$, and $\mathcal{G}_*^{\overline{\overline{\alpha}}}$ for $\alpha\in\mathcal{J}$. When the terms are collected and denoted in the aggregate as X, the result is identical in appearance to Eq. (C.33). The only difference is that here the entity set, $\mathcal{J}$, consists of seven members (w, n, s, wn, ws, ns, and wns) with their associated connected sets. The mathematical rearrangement of the equation is identical to the procession from Eq. (C.33) to Eq. (C.38). At this point, one could expand out the summations and then recombine them to obtain the entries in Eq. (11.5), as was done in obtaining Eq. (C.38). However, because there are seven entities, this expansion is quite lengthy. We will therefore use a more elegant approach.

First, we combine the first three pairs of summations in Eq. (C.37) into a single pair so that we have

$$\begin{aligned} X = \sum_{\alpha\in\mathcal{J}}\sum_{\kappa\in\mathcal{J}_{c\alpha}} &\left\{ \overset{\kappa\to\alpha}{Q} + \overset{\kappa\to\alpha}{G} + \overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}} + K_E^{\overline{\overline{\alpha,\kappa}}} + \psi^{\overline{\overline{\alpha,\kappa}}}\right) \right. \\ &\left. + \left[\overset{\kappa\to\alpha}{\mathbf{T}} + \overset{\kappa\to\alpha}{M}\left(\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}}{2}\right)\right]\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)\right\}\frac{1}{\theta^{\overline{\overline{\alpha}}}} \\ &- \sum_{\alpha\in\mathcal{J}}\sum_{\kappa\in\mathcal{J}_{c\alpha}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\overset{\kappa\to\alpha}{\mathbf{T}} - \overset{\kappa\to\alpha}{M}\left[\frac{\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}}{2} - \left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)\right]\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\,. \end{aligned} \tag{C.108}$$

We now break up this equation up by explicitly writing the sums over the connected sets, $\mathcal{J}_{c\alpha}$, as sums over $\mathcal{J}_{c\alpha}^-$ and $\mathcal{J}_{c\alpha}^+$. This yields

$$\begin{aligned} X = \sum_{\alpha\in\mathcal{J}}\sum_{\kappa\in\mathcal{J}_{c\alpha}^-} &\left\{ \overset{\kappa\to\alpha}{Q} + \overset{\kappa\to\alpha}{G} + \overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}} + K_E^{\overline{\overline{\alpha,\kappa}}} + \psi^{\overline{\overline{\alpha,\kappa}}}\right) \right. \\ &\left. + \left[\overset{\kappa\to\alpha}{\mathbf{T}} + \overset{\kappa\to\alpha}{M}\left(\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}}{2}\right)\right]\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)\right\}\frac{1}{\theta^{\overline{\overline{\alpha}}}} \\ + \sum_{\alpha\in\mathcal{J}}\sum_{\kappa\in\mathcal{J}_{c\alpha}^+} &\left\{ \overset{\kappa\to\alpha}{Q} + \overset{\kappa\to\alpha}{G} + \overset{\kappa\to\alpha}{M}\left(\overline{E}^{\overline{\overline{\alpha,\kappa}}} + K_E^{\overline{\overline{\alpha,\kappa}}} + \psi^{\overline{\overline{\alpha,\kappa}}}\right) \right. \\ &\left. + \left[\overset{\kappa\to\alpha}{\mathbf{T}} + \overset{\kappa\to\alpha}{M}\left(\frac{\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}}{2}\right)\right]\cdot\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)\right\}\frac{1}{\theta^{\overline{\overline{\alpha}}}} \end{aligned}$$

$$
\begin{aligned}
&-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}^{-}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\overset{\kappa\to\alpha}{\mathbf{T}}-\overset{\kappa\to\alpha}{M}\left[\frac{\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}}{2}-\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)\right]\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}^{+}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\overset{\kappa\to\alpha}{\mathbf{T}}-\overset{\kappa\to\alpha}{M}\left[\frac{\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}}{2}-\left(\mathbf{v}^{\overline{\overline{\alpha,\kappa}}}-\mathbf{v}^{\overline{s}}\right)\right]\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\,.
\end{aligned}
\tag{C.109}
$$

In the first double summation, we will make use of the fact that an exchange from κ to α is the negative of the exchange from α to κ and write all the exchange terms going from the higher dimensional entity to the lower, i.e., from α to κ. We will also make use of the fact that the double bar averages are of a higher dimensional property over the boundary. In the second double summation, we will exchange α with κ in all indices. Then we note that we can make use of the identity that applies here,

$$
\sum_{\kappa\in\mathfrak{J}}\sum_{\alpha\in\mathfrak{J}_{c\kappa}^{+}}\cdots=\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}^{-}}\cdots
\tag{C.110}
$$

In the third double summation, we change the leading sign from minus to plus and make all exchange term from α to κ. The last double summation is left unchanged except that the form of the double overbar average is made explicit. With these changes, we obtain

$$
\begin{aligned}
X=&-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}^{-}}\left\{\overset{\alpha\to\kappa}{Q}+\overset{\alpha\to\kappa}{G}+\overset{\alpha\to\kappa}{M}\left(\overline{E}_{\alpha}^{\overline{\kappa}}+K_{E\alpha}^{\overline{\overline{\kappa}}}+\psi_{\alpha}^{\overline{\kappa}}\right)\right.\\
&\left.\qquad+\left[\overset{\alpha\to\kappa}{\mathbf{T}}+\overset{\alpha\to\kappa}{M}\left(\frac{\mathbf{v}_{\alpha}^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}}{2}\right)\right]\cdot\left(\mathbf{v}_{\alpha}^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)\right\}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}^{-}}\left\{\overset{\alpha\to\kappa}{Q}+\overset{\alpha\to\kappa}{G}+\overset{\alpha\to\kappa}{M}\left(\overline{E}_{\alpha}^{\overline{\kappa}}+K_{E\alpha}^{\overline{\overline{\kappa}}}+\psi_{\alpha}^{\overline{\kappa}}\right)\right.\\
&\left.\qquad+\left[\overset{\alpha\to\kappa}{\mathbf{T}}+\overset{\alpha\to\kappa}{M}\left(\frac{\mathbf{v}_{\alpha}^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}}{2}\right)\right]\cdot\left(\mathbf{v}_{\alpha}^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)\right\}\frac{1}{\theta^{\overline{\overline{\kappa}}}}\\
&+\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}^{-}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\overset{\alpha\to\kappa}{\mathbf{T}}-\overset{\alpha\to\kappa}{M}\left[\frac{\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}}{2}-\left(\mathbf{v}_{\alpha}^{\overline{\kappa}}-\mathbf{v}^{\overline{s}}\right)\right]\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\\
&-\sum_{\alpha\in\mathfrak{J}}\sum_{\kappa\in\mathfrak{J}_{c\alpha}^{+}}\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\{\overset{\kappa\to\alpha}{\mathbf{T}}-\overset{\kappa\to\alpha}{M}\left[\frac{\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}}{2}-\left(\mathbf{v}_{\kappa}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\right]\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\,.
\end{aligned}
\tag{C.111}
$$

The first double summation is the same as the second except for the inverse temperature factor. Thus, these summations are easily combined, leading to the needed expression

$$
\begin{aligned}
X = & - \sum_{\alpha \in \mathfrak{J}} \sum_{\kappa \in \mathfrak{J}_{c\alpha}^{-}} \left\{ \underbrace{\overset{\alpha\to\kappa}{Q} + \overset{\alpha\to\kappa}{G} + \overset{\alpha\to\kappa}{M} \left(\overline{E}_{\alpha}^{\overline{\kappa}} + K_{E\alpha}^{\overline{\overline{\kappa}}} + \psi_{\alpha}^{\overline{\kappa}} \right)}_{18,21,24} \right. \\
& \left. \underbrace{+ \left[\overset{\alpha\to\kappa}{\mathbf{T}} + \overset{\alpha\to\kappa}{M} \left(\frac{\mathbf{v}_{\alpha}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}}}{2} \right) \right] \cdot \left(\mathbf{v}_{\alpha}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right)}_{19,22,25} \right\} \underbrace{\left(\frac{1}{\theta^{\overline{\overline{\alpha}}}} - \frac{1}{\theta^{\overline{\overline{\kappa}}}} \right)}_{20,23,26} \\
& + \sum_{\alpha \in \mathfrak{J}} \underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}}_{29,31} \underbrace{\sum_{\kappa \in \mathfrak{J}_{c\alpha}^{-}} \left\{ \overset{\alpha\to\kappa}{\mathbf{T}} - \overset{\alpha\to\kappa}{M} \left[\frac{\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}}{2} - \left(\mathbf{v}_{\alpha}^{\overline{\kappa}} - \mathbf{v}^{\overline{s}} \right) \right] \right\}}_{30,33} \cdot \underbrace{\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right)}_{30,35} \\
& - \sum_{\alpha \in \mathfrak{J}} \underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}}_{31,36} \underbrace{\sum_{\kappa \in \mathfrak{J}_{c\alpha}^{+}} \left\{ \overset{\kappa\to\alpha}{\mathbf{T}} - \overset{\kappa\to\alpha}{M} \left[\frac{\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}}{2} - \left(\mathbf{v}_{\kappa}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right) \right] \right\}}_{32,38} \cdot \underbrace{\left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}} \right)}_{35,41} .
\end{aligned}
\tag{C.112}
$$

Lines 27 and 28

These lines account for the concentrated stress and heat conduction between the solid phase and the common curve. The elements of these lines are found in $\mathcal{E}_{*}^{\overline{\overline{s}}}$, $\mathcal{E}_{*}^{\overline{\overline{wns}}}$, $\boldsymbol{\mathcal{P}}_{*}^{\overline{\overline{s}}}$, $\boldsymbol{\mathcal{P}}_{*}^{\overline{\overline{wns}}}$, and $\mathcal{T}_{*}^{\overline{\overline{s}}}$. The part of the concentrated stress that comes from $\mathcal{T}_{*}^{\overline{\overline{s}}}$ is written within an averaging operator that cannot be evaluated exactly. Therefore, to ensure that all terms will be combined in the most useful fashion, we will make use of the identity of Eq. (6.98) which provides

$$
\overset{wns\to s}{\mathbf{T}^{*}} = \langle \mathbf{t}_{s}^{*} \cdot \mathbf{n}_{s} \rangle_{\Omega_{wns},\Omega} . \tag{C.113}
$$

The terms are collected in the order in which they appear in Eq. (C.82) in the following, and the substitution of Eq. (C.113) is employed to obtain

$$
\begin{aligned}
& \left(\overset{wns\to s}{\mathbf{T}^{*}} \cdot \mathbf{v}_{s}^{\overline{\overline{wns}}} + \overset{wns\to s}{Q^{*}} \right) \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}} \right) \\
& \quad - \overset{wns\to s}{\mathbf{T}^{*}} \cdot \left(\frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}} - \frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{wns}}}} \right) - \frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_{s} \cdot \mathbf{t}_{s}^{*} \cdot \left(\mathbf{v}_{s} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega} \\
= & \left(\langle \mathbf{t}_{s}^{*} \cdot \mathbf{n}_{s} \rangle_{\Omega_{wns},\Omega} \cdot \mathbf{v}_{s}^{\overline{\overline{wns}}} + \overset{wns\to s}{Q^{*}} \right) \left(\frac{1}{\theta^{\overline{\overline{s}}}} - \frac{1}{\theta^{\overline{\overline{wns}}}} \right) \\
& \quad - \langle \mathbf{t}_{s}^{*} \cdot \mathbf{n}_{s} \rangle_{\Omega_{wns},\Omega} \cdot \left(\frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}} - \frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{wns}}}} \right) - \frac{1}{\theta^{\overline{\overline{s}}}} \left\langle \mathbf{n}_{s} \cdot \mathbf{t}_{s}^{*} \cdot \left(\mathbf{v}_{s} - \mathbf{v}^{\overline{s}} \right) \right\rangle_{\Omega_{wns},\Omega} .
\end{aligned}
\tag{C.114}
$$

The terms on the right side are then rearranged to the expressions that are needed for Eq. (11.5) according to

$$
\begin{aligned}
&\left(\overset{wns\to s}{\mathbf{T}^*}\cdot\mathbf{v}_s^{\overline{\overline{wns}}}+\overset{wns\to s}{Q^*}\right)\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)\\
&\quad-\overset{wns\to s}{\mathbf{T}^*}\cdot\left(\frac{\mathbf{v}^{\overline{s}}}{\theta^{\overline{\overline{s}}}}-\frac{\mathbf{v}^{\overline{wns}}}{\theta^{\overline{\overline{wns}}}}\right)-\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\left(\mathbf{v}_s-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}\\
&=\underbrace{\left[\overset{wns\to s}{Q^*}+\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\left(\mathbf{v}_s^{\overline{wns}}-\mathbf{v}_s\right)\right\rangle_{\Omega_{wns},\Omega}\right.}_{27}\\
&\quad\underbrace{\left.+\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\left(\mathbf{v}_s-\mathbf{v}_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}\right]\left(\frac{1}{\theta^{\overline{\overline{s}}}}-\frac{1}{\theta^{\overline{\overline{wns}}}}\right)}_{28}\\
&+\underbrace{\frac{1}{\theta^{\overline{\overline{wns}}}}}_{36}\underbrace{\left\langle\mathbf{t}_s^*\cdot\mathbf{n}_s\right\rangle_{\Omega_{wns},\Omega}\cdot\left(\mathbf{v}^{\overline{wns}}-\mathbf{v}^{\overline{s}}\right)}_{41}-\underbrace{\frac{1}{\theta^{\overline{\overline{wns}}}}}_{48}\underbrace{\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\left(\mathbf{v}_{wns}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{wns},\Omega}}_{49}\\
&-\underbrace{\frac{1}{\theta^{\overline{\overline{s}}}}\left\langle\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\left(\mathbf{v}_s-\mathbf{v}_{wns}\right)\right\rangle_{\Omega_{wns},\Omega}}_{50}\ .
\end{aligned}
\tag{C.115}
$$

Lines 29–41

Lines 29 and 30 accumulate terms that multiply $\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}$ for $\alpha\in\mathcal{J}_\mathrm{f}$. Many of these terms have already been provided from Eqs. (C.84), (C.89), and (C.112). The remaining terms are provided directly, without further rearrangement from $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$ with $\alpha\in\{w,n\}$, in Eq. (C.82).

Terms that multiply the difference between the interface and solid velocities, $\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}$ for $\alpha\in\mathcal{J}_\mathrm{I}$, appear in lines 31–35. Parts of these lines have already been assembled from Eqs. (C.86), (C.91), and (C.112). Additional terms come from $\mathcal{T}_*^{\overline{\overline{\alpha}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{\alpha}}}$ with $\alpha\in\{wn,ws,ns\}$ in Eq. (C.82). These terms have to be rearranged. The collected terms are on the left of the following equation, and their rearranged forms that appear in Eq. (11.5) are given on the right side,

$$
\begin{aligned}
&\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\eta_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}}\\
&\quad+\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\mu^{\overline{\alpha}}\\
&\quad+\frac{1}{\theta^{\overline{\overline{\alpha}}}}\left\langle\rho_\alpha\left(\mathbf{v}_\alpha-\mathbf{v}^{\overline{s}}\right)\cdot\left(\mathsf{I}-\mathsf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\psi^{\overline{i\alpha}}\\
&=\underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}}_{31}\underbrace{\left[\left\langle\eta_\alpha\left(\mathsf{I}-\mathsf{I}'_\alpha\right)\right\rangle_{\Omega_\alpha,\Omega}\cdot\nabla\theta^{\overline{\overline{\alpha}}}\right]}_{34}\cdot\underbrace{\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)}_{35}
\end{aligned}
$$

$$
\begin{aligned}
&+ \underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\langle \eta_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha\right) \right\rangle_{\Omega_\alpha,\Omega} \cdot \nabla \theta^{\overline{\overline{\alpha}}}}_{53} \\
&+ \underbrace{\frac{1}{\theta^{\overline{\overline{\alpha}}}}}_{31} \underbrace{\left[\left\langle \rho_\alpha \left(\mathsf{I} - \mathsf{I}'_\alpha\right) \right\rangle_{\Omega_\alpha,\Omega} \cdot \nabla \left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}}\right) \right] \cdot \left(\mathbf{v}^{\overline{\alpha}} - \mathbf{v}^{\overline{s}}\right)}_{35} \\
&\underbrace{+ \frac{1}{\theta^{\overline{\overline{\alpha}}}} \left\langle \rho_\alpha \left(\mathbf{v}_\alpha - \mathbf{v}^{\overline{\alpha}}\right) \cdot \left(\mathsf{I} - \mathsf{I}'_\alpha\right) \right\rangle_{\Omega_\alpha,\Omega} \cdot \nabla \left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}}\right)}_{55} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{I}} \,. \qquad \text{(C.116)}
\end{aligned}
$$

Lines 36–41 consist of terms that multiply the difference between the common curve and solid velocities, $\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}$. Contributions to these lines have been made in earlier manipulations as given in Eqs. (C.88), (C.92), (C.112), and (C.115). Additional terms come from $\mathcal{T}_*^{\overline{\overline{wns}}}$ and $\mathcal{T}_{\mathcal{G}*}^{\overline{\overline{wns}}}$ with rearrangements required. The contributed terms on the left are rearranged to the expressions on the right in the following equation, and these are placed in Eq. (11.5):

$$
\begin{aligned}
&\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}} \left\langle \eta_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}''_{wns}\right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \theta^{\overline{\overline{\overline{wns}}}} \\
&\quad + \frac{1}{\theta^{\overline{\overline{\overline{wns}}}}} \left\langle \rho_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}''_{wns}\right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \mu^{\overline{wns}} \\
&\quad + \frac{1}{\theta^{\overline{\overline{\overline{wns}}}}} \left\langle \rho_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}\right) \cdot \left(\mathsf{I} - \mathsf{I}''_{wns}\right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \psi^{\overline{iwns}} \\
&= \underbrace{\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}}_{36} \underbrace{\left[\left\langle \eta_{wns} \left(\mathsf{I} - \mathsf{I}''_{wns}\right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \theta^{\overline{\overline{\overline{wns}}}} \right]}_{39} \cdot \underbrace{\left(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right)}_{41} \\
&\quad + \underbrace{\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}} \left\langle \eta_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}}\right) \cdot \left(\mathsf{I} - \mathsf{I}''_{wns}\right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \theta^{\overline{\overline{\overline{wns}}}}}_{56} \\
&\quad + \underbrace{\frac{1}{\theta^{\overline{\overline{\overline{wns}}}}}}_{36} \underbrace{\left[\left\langle \rho_{wns} \left(\mathsf{I} - \mathsf{I}''_{wns}\right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \left(\mu^{\overline{wns}} + \psi^{\overline{wns}}\right) \right]}_{40} \cdot \underbrace{\left(\mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}}\right)}_{41} \\
&\quad \underbrace{+ \frac{1}{\theta^{\overline{\overline{\overline{wns}}}}} \left\langle \rho_{wns} \left(\mathbf{v}_{wns} - \mathbf{v}^{\overline{wns}}\right) \cdot \left(\mathsf{I} - \mathsf{I}''_{wns}\right) \right\rangle_{\Omega_{wns},\Omega} \cdot \nabla \left(\mu^{\overline{wns}} + \psi^{\overline{wns}}\right)}_{58} \,. \qquad \text{(C.117)}
\end{aligned}
$$

Lines 42–49

These lines are averages of the product of a microscale force with a microscale flux where both factors are zero at equilibrium. Some of the terms in these equations have already been developed while others are provided directly from elements of Eq. (C.82) without additional rearrangement. The origins of these lines are:

Lines 42 and 43: Eqs. (C.91), (C.106), and a term from $\mathcal{T}_{*}^{wn}$;
Lines 44 and 45: Eqs. (C.91), (C.104), (C.106), and a term from $\mathcal{T}_{*}^{ws}$;
Lines 46 and 47: Eqs. (C.91), (C.104), (C.106), and a term from $\mathcal{T}_{*}^{ns}$; and
Lines 48 and 49: Eqs. (C.92), (C.107), (C.115), and a term from $\mathcal{T}_{*}^{wns}$.

Lines 50–59

All these terms have either been developed as a byproduct of consideration of previous lines or are pulled in directly from Eq. (C.82). In brief, the sources of the terms are as follows:

Lines 50 and 51: Eqs. (C.115) and (C.104);
Line 52: This is obtained directly from $\mathcal{T}_{*}^{\overline{\overline{s}}}$;
Lines 53–58: Eqs. (C.86), (C.88), (C.116), and (C.117); and
Line 59: This is obtained directly from $\mathcal{S}_{*}^{\overline{\overline{s}}}$.

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